

DESIGN AND COST ESTIMATION FOR DESALTING
TETRAETHYLENE GLYCOL USING
ION-EXCHANGE

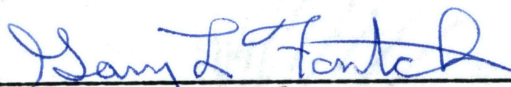
By
KALAGA SUDHAKAR
Bachelor of Technology
Osmania University
Hyderabad, India
1989

Submitted to the faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1990

Thesis
1990
K144
cop. 2

DESIGN AND COST ESTIMATION FOR DESALTING
TETRAETHYLENE GLYCOL USING
ION-EXCHANGE

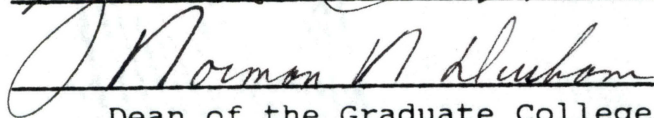
Thesis Approved:



Thesis Adviser







Dean of the Graduate College

PREFACE

Desalting of Tetraethylene Glycol using ion-exchange was studied. For the study Batch and Column experiments were performed using different ion-exchange resins by changing parameters such as Temperature, Water content, and the order of the the ion-exchange resins used. Based on the experimental results design and cost estimation of a desalting plant operating at temperature of 180⁰F and 220⁰F were proposed. This process can also be used for other operating temperatures.

I wish to express my sincere gratitude to the individuals who assisted me in this project and during my course work at Oklahoma State University. In particular, I wish to thank my major adviser, Dr. Gary L. Foutch, for his invaluable guidance, inspiration, and patience. I am also thankful to Dr. Ruth C. Erbar and Dr. Edward J. Zecchini, for serving on my graduate committee.

I am grateful to Phillips Petroleum for the financial support I received during this project.

My deepest appreciation is extended to my parents, my brothers, my sister, and my uncle Dr. Y. Gopal Krishna for their love, support, moral encouragement, and understanding.

This work is solely dedicated to my mother.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	5
III. EXPERIMENTAL PROCEDURE.....	8
IV. RESULTS AND DISCUSSION.....	10
V. PROCESS DESIGN AND COST ESTIMATION.....	28
Equipment and Material Sizing.....	33
Cation Exchange Column.....	34
Anion Exchange Column.....	34
Regenerants Requirements.....	35
Resin Requirements.....	35
Heat Exchanger.....	36
Cost Estimation.....	37
VI. CONCLUSIONS AND RECOMMENDATIONS.....	45
Conclusions.....	45
Recommendations.....	46
BIBLIOGRAPHY.....	48
APPENDIXES	
APPENDIX A - EXPERIMENTAL DATA	50
APPENDIX B - EQUIPMENT SIZING AND COST ESTIMATION.....	79
APPENDIX C - CALCULATION OF RUN TIME.....	85
APPENDIX D - EXPERIMENTAL ERROR.....	88

LIST OF TABLES

Table	Page
1. Characteristics of Ion Exchange Columns.....	35
2. Cost Estimation of Ion Exchange Process at 180°F with Regeneration.....	38
3. Cost Estimation of Ion Exchange Process at 180°F and Contracting out for Regeneration.....	40
4. Cost Estimation for Ion Exchange Process at 220°F with Incineration of Resin each time.....	42
5. Comparative Costs of Ion Exchange Processes.....	44
6. pH Change Versus Time For Batch Experiment At 74°F For TEG With 10% Water Using Anion Treatment First.....	51
7. pH Change Versus Time For Batch Experiment At 74°F For TEG With 10% Water Using Cation Treatment First.....	52
8. pH Change Versus Time For Batch Experiment At 74°F For TEG With 20% Water Using Cation Treatment First.....	53
9. pH Change Versus Time For Batch Experiment At 74°F For TEG With 20% Water Using Anion Treatment First.....	54
10. pH Change Versus Time For Batch Experiment At 100°F For TEG With 10% Water Using Cation Treatment First.....	55
11. pH Change Versus Time For Batch Experiment At 100°F For TEG With 20% Water Using Cation Treatment First.....	56
12. pH Change Versus Time For Batch Experiment At 100°F For TEG With 10% Water Using Anion Treatment First.....	57
13. pH Change Versus Time For Batch Experiment At 100°F For TEG With 20% Water Using Anion Treatment First.....	58

Table	Page
14. pH Change Versus Time For Batch Experiment At 120°F For TEG With 10% Water Using Cation Treatment First.....	59
15. pH Change Versus Time For Batch Experiment At 120°F For TEG With 20% Water Using Cation Treatment First.....	60
16. pH Change Versus Time For Batch Experiment At 120°F For TEG With 10% Water Using Anion Treatment First.....	61
17. pH Change Versus Time For Batch Experiment At 120°F For TEG With 20% Water Using Anion Treatment First.....	62
18. pH Change Versus Time For Batch Experiment At 140°F For TEG With 20% Water Using Cation Treatment First.....	63
19. pH Change Versus Time For Batch Experiment At 140°F For TEG With 20% Water Using Anion Treatment First.....	64
20. pH Change Versus Time For Batch Experiment At 140°F For TEG With 20% Water Using Cation (Amberlyst 15) Treatment First.....	65
21. pH Change Versus Time For Batch Experiment At 140°F For TEG With 20% Water Using Anion (Amberlyst 21) Treatment First.....	66
22. Rate Constants for Batch Experiments for TEG with 10% and 20% Water at different temperatures using Anion Treatment first.....	67
23. Rate Constants for Batch Experiments for TEG with 10% and 20% Water at different temperatures using Cation Treatment first.....	68
24. Rate Constants for Batch Experiments for TEG with 10% and 20% Water at different temperatures using Anion Treatment for Cation Treated solution.....	69
25. Rate Constants for Batch Experiments for TEG with 10% and 20% Water at different temperatures using Cation Treatment for Anion Treated solution.....	70
26. Analysis of Batch Experiment Samples using Ion-Chromatograph, and Experimental Error.....	71

Table	Page
27. Volume collected and Concentration change with Time for 500ml TEG without Water having an Initial Concentration of 330ppm of Chloride Ions in a Column Experiment using 5.0gr of Cation and Anion Resins each with a Residence time of 2 minutes.....	72
28. Volume collected and Concentration change with Time for 750ml TEG with 15% Water having an initial concentration of 330ppm of Chloride Ions in a Column Experiment using 5.0gr of Cation and Anion Resins each with a Residence time of 2 minutes.....	73
29. Ion-Chromatography Calibration.....	74
30. pH Change Versus Time For Batch Experiments At 74 ^o F for TEG With 20% Water Using Wet, Soaked, and Dry Resins With Cation First.....	75
31. Average, Minimum, and Maximum Peak Heights of the TEG Samples in the Analysis Using Ion-Chromatography.....	91

LIST OF FIGURES

Figure	Page
1. pH _{initial} /pH Versus Time For Batch Experiment At 140°F With 20% Water Using Cation Treatment First For TEG.....	11
2. pH _{initial} /pH Versus Time For Batch Experiment At 140°F With 20% Water Using Anion Treatment For Cation Treated TEG	13
3. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 10% Water Using Cation Treatment First And Anion Treatment First.....	14
4. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 10% Water Using Cation Treatment For Anion Treated Solution And Anion treatment For Cation Treated Solution.....	15
5. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 20% Water Using Cation Treatment first And Anion Treatment First.....	16
6. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 20% Water Using Cation Treatment For Anion Treated Solution And Anion treatment For Cation Treated Solution.....	17
7. Effect Of Temperature On Lag Times For Batch Experiments For TEG With 10% And 20% Water Using Cation Treatment For Anion Treated Solution And Anion Treatment For Cation Treated Solution.....	19
8. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 10% Water Using Anion Treatment First.....	20
9. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 10% Water Using Cation Treatment First.....	21

Figure	Page
10. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 20% Water Using Anion Treatment First.....	22
11. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 20% Water Using Cation Treatment First.....	23
12. Breakthrough Curves For Column Experiments For TEG Without Water And With 15% Water Using Cation Treatment Followed By Anion Treatment.....	24
13. Time Versus pH Change For Batch Experiments For TEG With 20% Water At Room Temperature Using Wet, Dry, And Resins Soaked In Pure TEG With Cationic Treatment First.....	26
14. Time Versus pH Change For Batch Experiments For TEG With 20% Water At Room Temperature Using Wet, Dry, And Resins Soaked In Pure TEG With Anionic Treatment For Cation Treated Solution.....	27
15. Flow Chart For TEG Stream Purification.....	29
16. Plant Layout For Ion-Exchange Process At 180°F.....	31
17. Plant Layout For Ion-Exchange Process At 220°F.....	32
18. Ion-Chromatograph Calibration	76
19. pH Change Versus Time For Batch Experiment For TEG With 20% Water At 140°F Using Cation Treatment First.....	77
20. pH Change Versus Time For Batch Experiment For TEG With 20% Water At 140°F Using Anion Treatment For Cation Treated Solution.....	78

CHAPTER I

INTRODUCTION

Natural gas is a major source of energy. Crude natural gas from oil wells carries water and other contaminants. The water present with crude natural gas forms hydrates, which results in high pressure drops in the flow pipes during long distance transport, and causes problems in gas lift valves during the pumping of oil using natural gas (5). The formation of hydrates can be prevented by dehumidification of crude natural gas.

Dehumidification is done by absorption of water with a suitable solvent, usually a glycol (7). Dehumidification efficiency depends on the high concentrations of glycols, approaching 99.9% (2). These high concentrations are usually achieved by evaporating water from the glycol in recycling units.

Different glycols are used depending upon the composition of the natural gas and the process used. Diethylene glycol, triethylene glycol, and tetraethylene glycol are suitable absorbants. Triethylene glycol is preferred in most applications. Diethylene glycol continues to find favor in vacuum regeneration type absorption units, and in mixed glycol-amine processes, which sweeten and dehydrate simultaneously. Tetraethylene

glycol is used mostly in dehydration of high temperature gas streams, due to lower glycol vaporization losses (5).

The water vapor, carried by natural gas, is absorbed continuously from the process gas stream by countercurrent contact with highly concentrated glycol in a packed or bubble tray column. Rich glycol, for recycling, flows to a combined glycol still and reboiler, in which glycol concentration is increased to approximately 99 % by atmospheric boiling at 400⁰F. The glycol is then flashed across a throttling valve to vacuum, then reheated to 400⁰F, and separated in a vacuum drum, thus yielding glycol concentrations as high as 99.9% (9).

Natural gas containing water also carries dissolved mineral salts, predominantly sodium chloride (4). This results in gradual accumulation of a significant amount of salts in the liquid phase during the dehumidification process. These soluble salts decrease the absorbing capacity of the glycol after its recycling. Moreover, during recycling, these salts cause corrosion in the equipment by forming salt sediments in the hot channels. In addition, excessive heat losses by scale formation over the heat transfer area are observed. In order to restore glycol absorption ability and to prevent the expensive equipment damages, the glycol has to be desalted.

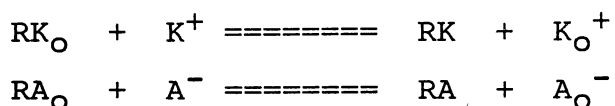
The current methods of desalting are (4):

1. Precipitating the salts chemically and removing the sediments by filtration or decantation,
2. Electrolysis or electrodialysis of the salt solution,

3. Decreasing salt solubility by water evaporation,
4. Removal of salts using ion-exchangers.

The desired characteristics for desalination are, effectiveness, non-complicated, flexibility, and low operating costs.

The ion-exchange method is simple, effective and inexpensive. The resins are a multimolecular substance (iontes), either cation-exchangers or anion-exchangers. The general representation of these reactions are,



Where R is the ionite, K_O^+ and A_O^- are mobile cations and anions respectively, and K^+ and A^- are electrolyte ions (4). Ion-exchange may also take part between ions of different valences, but the stoichiometric relation must be satisfied. In order to regenerate the exchangers to their initial form, the reverse reaction must occur. In the ionic-regeneration step, sulfuric acid and sodium hydroxide force the reactions in the reverse direction. The structure of the ionites should be sufficiently porous and permeable to the solution as well as ions to allow diffusion.

Ion-exchange technology has been applied to the desalting of diethylene glycol, but the application to tetraethylene glycol is new (4). The process of desalting tetraethylene glycol by using ion-exchange may be as follows:

1. Removal of mechanical impurities or other solids built-up during dehydration by using a membrane or

charcoal filter (4),

2. Exchange of cations on the cationate,
3. Exchange of anions on the anionate, and
4. Regeneration of saturated ionites.

The process stream, tetraethylene glycol, essentially contains Na^+ , Mg^{++} , Ca^{++} and Cl^- . The above ion-exchange process has been studied in the laboratory to reduce the ionic concentration of Cl^- in the TEG from 825/ppm to 25/ppm and thus significantly reduce corrosion problems caused by the dissolved salts. Preliminary experiments to evaluate temperature, water content, and the order of ion-exchanger used in a batch reactor are performed. Samples were collected for analysis of residual salts using a Dionex 2000i/sp exchange chromatograph. Based on these analyses, a column is designed for a continuous desalting process. Implementation of this ion-exchange process will result in a substantial reduction of ionic impurities in the process TEG stream. This will solve corrosion and fouling problems in process equipment.

CHAPTER II

LITERATURE REVIEW

Since high concentration glycol regeneration was introduced in 1957, hundreds of glycol dehydration plants have been installed worldwide. Since this process began however, corrosion problems have been observed with plant equipment. This has been the subject of several investigations.

Extensive studies were performed by Lloyd and Taylor (6) on the chemical factors effecting corrosion by aqueous glycol solutions and some means of controlling this corrosion. During this process, the glycol, containing a high percentage of water, is subjected to elevated temperature and cumulative exposure to the impurities in the feed stream, like traces of light acids and oxygen. Consequently, in the absence of effective corrosion control, steel equipment may develop serious problems over a period of time. Lloyd and Taylor conclude, (1) corrosion of equipment in contact with a glycol solution is negligible as compared with that of vapor condensates, (2) the corrosion rate increased with a decrease in pH, (3) at elevated temperatures (185°F) glycol autoxidizes in air forming aldehydes and acids, and increases corrosion, and (4) glycol made alkaline by adding 0.03% of monoethanolamine (MEA) showed fairly low corrosion.

Low temperature methods of gas preparation with the addition and regeneration of glycol has become very common (1). But after several years, operation of low temperature separation plants showed corrosion problems. Recent research indicates that the corrosion problem in the dehydration unit is caused by the mineral salts present in the water carried by natural gas rather than the autoxidation of glycol. Desalination of the treated glycol, and many different methods of desalination were proposed by Masteynek et al (4). Matvenko and Yarym-Agaev (3) proposed a technological procedure for desalting diethylene glycol by benzene. Desalting of solvents using ion-exchange is not new. Many studies were made for desalting of different glycols, viz., ethylene glycol, diethylene glycol, triethylene glycol, and polyethylene glycol using ion exchangers and successfully implemented in process plants. However no literature is available for tetraethylene glycol desalting using ion-exchangers.

Gritsenko, et al(1) and Masteynek, et al(4) have conducted laboratory experiments for removing salts from diethyl glycol using ion-exchangers. The glycol was passed through three filters: a mechanical filter, a cation exchange filter and an anion exchange filter. The mechanical filter consists of packed thio-carbonate, intended to remove dirt and mechanical impurities from diethylene glycol. The cation and anion exchange filter consists of packed KU-2 cation exchange and AV-17 anion exchange resins, respectively. These are intended to remove sodium and chloride. The saturated cation

exchangers and anion exchangers were regenerated with one percent sulfuric acid and four percent sodium hydroxide, respectively. After passing through cationic exchangers, the pH of diethylene glycol dropped to about one. After the anion exchanger, the final pH of diethylene glycol ranged from about seven to nine. By this method they could reduce the salts (NaCl) from 20.8 g/l to 2.1 g/l. They also found that if the cation exchanger is regenerated with 5% ammonium chloride solution (NH_4Cl), the pH of the diethylene glycol remained at six to seven and there was no longer a need for the anion exchange filter. Mastenek, et al.(4) also proposed that at high salt content (80-90 gms/lit), it is initially necessary to desalt diethylene glycol by heating to 100°C - 120°C . At this temperature the solubility of NaCl decreases and the salt settles at the bottom of the reservoir. The diethylene glycol desalted initially is subjected to the usual desalting process using ion-exchangers.

The solubility characteristics of salts in a particular solvent have been shown to be important before desalting. Chianese, et al.(7) studied the solubility of NaCl in the glycol-water mixture. They concluded that for solvent composition in the range of 50-80 wt% diethylene glycol, temperature exhibits little or no influence over NaCl solubility, and the solubility of NaCl decreases with an increase in temperature of pure glycol solutions.

CHAPTER III

EXPERIMENTAL PROCEDURE

The experimental procedure for desalting of tetraethylene glycol using ion-exchange resins is primarily divided into three parts: preliminary experiments, analysis of samples for residual salts, and column experiments.

Preliminary batch experiments were carried out in a 250 ml beaker. Thirty-two experiments were performed at four different temperatures (room temperature, 100, 120, and 140°F), at two different water compositions (10% by volume and 20% by volume), and at different orders of resin used (anion first, and cation later). All initial experiments were performed in a baffled 250 ml beaker using a mechanical stirrer. The temperature of the beaker is maintained within $\pm 1.0^{\circ}\text{F}$ using a waterbath. For all these preliminary experiments water and Amberlite 200 H and Amberlite 900 OH resins and 200 ml of tetraethylene glycol were used. Also Amberlyst A-21 and Amberlyst 15 resins were used for comparison. About six grams of ion-exchange resin (about five fold excess capacity) is used for the solution initially. The concentration versus time data is obtained by monitoring the pH change, which is proportional to the change in concentration of the dissociated ions of the salts. The pH change is monitored

with an Orion Research Ionalyzer model 407A pH meter, until equilibrium is reached. Tetraethylene glycol is separated from the resin using Whattman filter paper and collected for analysis. The resin is stored for regeneration.

Adsorption by filter paper is assumed negligible.

Samples are analyzed for residual salts by ion chromatography (DIONEX 2000 spi). The tetraethylene glycol samples are diluted to one percent to prevent damage to the analytic column. A calibration plot of concentration verses peak height for standard samples is generated. The qualitative and quantitative analysis of the samples is done by comparing the retention times and peak heights with standards. All the samples were analysed in single run and IC calibration was done each time.

The results from the above experiments are used to develop a suitable column design for a continuous process that can be used for industrial applications. Laboratory scale column experiments were conducted with a half inch column at room temperature, gravity feed, with 5-10 grams of resin, and 750 ml of tetraethylene glycol. The effluent samples are collected with time for analysis.

CHAPTER IV

RESULTS AND DISCUSSION

In this section, the effects of temperature, water content and the order of the resin on desalting of tetraethylene glycol will be presented.

Raw data for the batch experiments for different conditions of temperature, water content, and the order of the resin are listed in Tables 6 through 21 in Appendix A. These tables list the pH change with time for four different temperatures i.e., Room temperature, 100°F, 120°F, and 140°F with 10% and 20% water content in the TEG, and by changing the order of the resin. The experiments were named according to the conditions at which they were conducted. For example C-T140-W20 indicates cationic treatment followed by anionic treatment at 140°F temperature and with 20% water content.

For the experiments listed in Tables 6 through 21, a plot of $\ln (\text{pH initial}/\text{pH})$ verses time showed a linear relationship. Figure 1 is a plot for the cationic treatment of Experiment C-T140-W20. This showed a rapid pH change initially which slowed down later. The region where pH change is slow shows the attainment of equilibrium. The same trend was observed for Experiments 1 to 16. The linear relationship confirms first order reaction for the ion-exchange process.

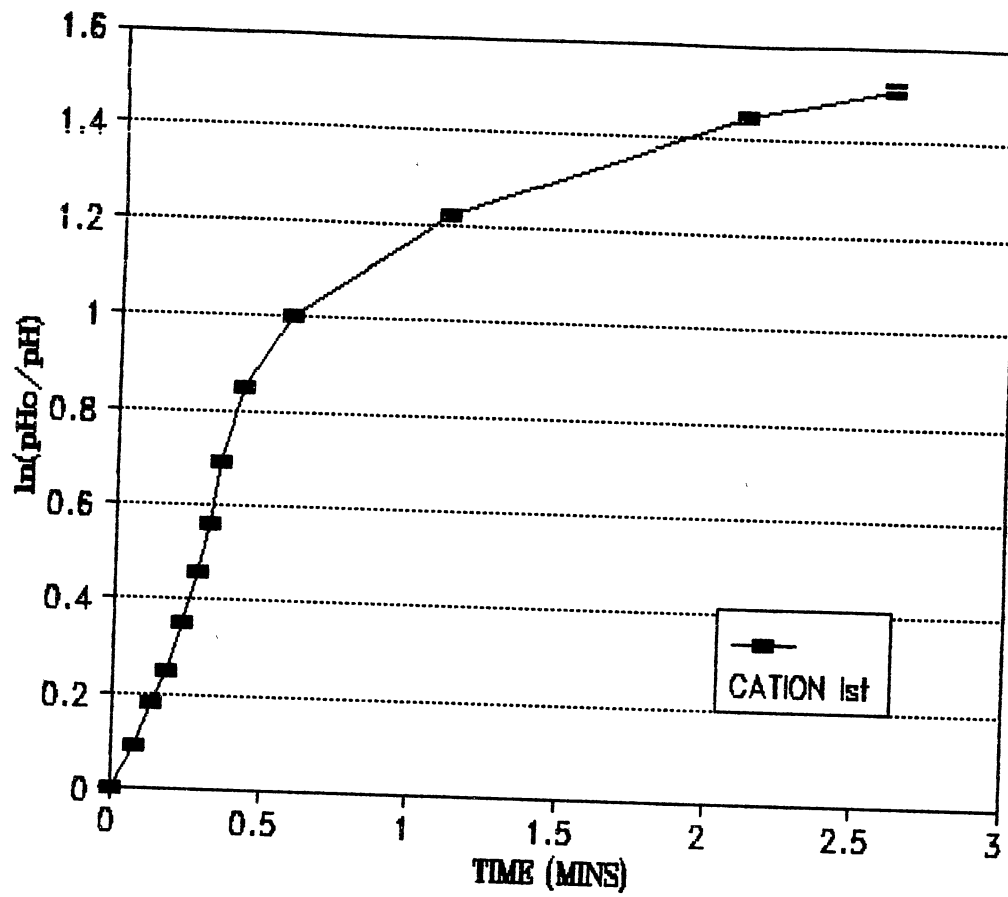


Figure 1. $\text{pH}_{\text{initial}}/\text{pH}$ Versus Time For Batch
Experiment At 140°F With 20% Water
Using Cation Treatment First For TEG

The anionic treatment for cation treated solution also showed the same linear relation for the plot of $\ln(pH_{\text{initial}}/pH)$ versus time (Fig 2). From the plot it can be seen there is an initial lag time.

The rate constants for ion-exchange reactions for Experiments 1 to 16 are calculated from the plots $\ln(pH_o/pH)$ versus time. The rate constant is given by the slope of the line. For calculating the rate constants, the data points from the region of rapid pH change are regressed. The rate constants for these experiments are listed in Tables 22 to 25 (Appendix A).

Figure 3 shows that the rate constants increase with temperature for anion first with 10% water content TEG. It did not show a definite trend with temperature for cation first treatment with 10% water content.

Figure 4 shows that the reaction constant has no effect with temperature for anion treatment of cation treated 10% water TEG. The cation treatment of anion treated 10% water TEG shows an increase with temperature. From Figures 3 and 4 it can be seen that the anion treatment followed by cation treatment has shown an increase in rate with temperature, while cation treatment followed by anion treatment has shown little effect with temperature. Figures 5 and 6 show a similar effect of temperature compared to Figures 3 and 4, respectively. It shows that addition of water has no significant effect on the rate constants.

Lag time was observed for anion treatment of cation treated solution and cation treatment of anion treated

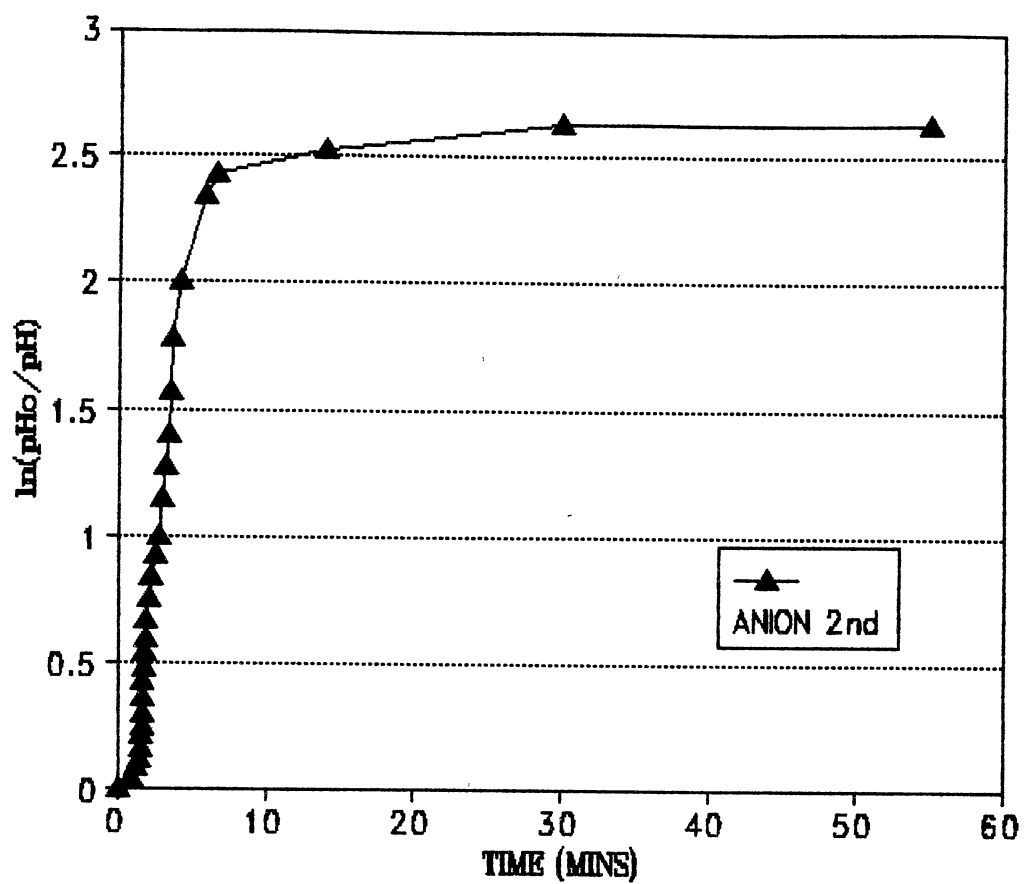


Figure 2. $\text{pH}_{\text{initial}}/\text{pH}$ Versus Time For Batch Experiment At 140°F With 20% Water Using Anion Treatment For Cation Treated TEG

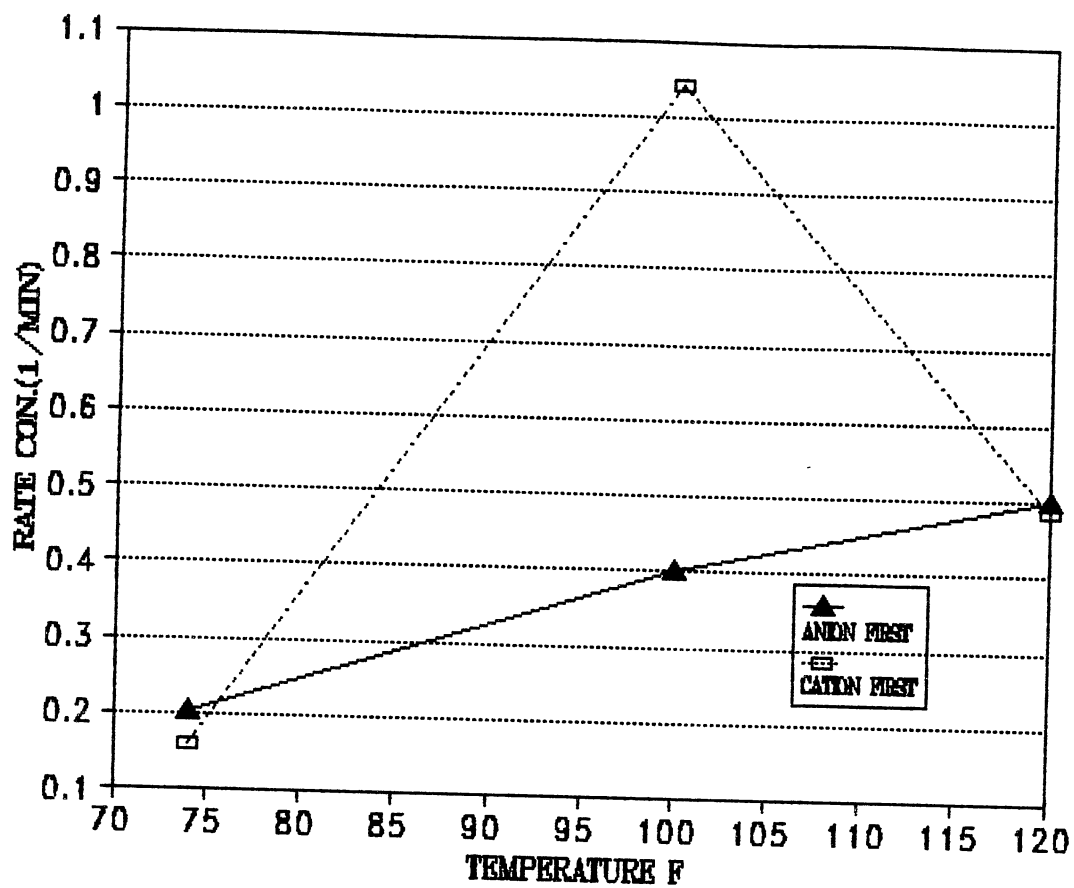


Figure 3. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 10% Water Using Cation Treatment First And Anion Treatment First

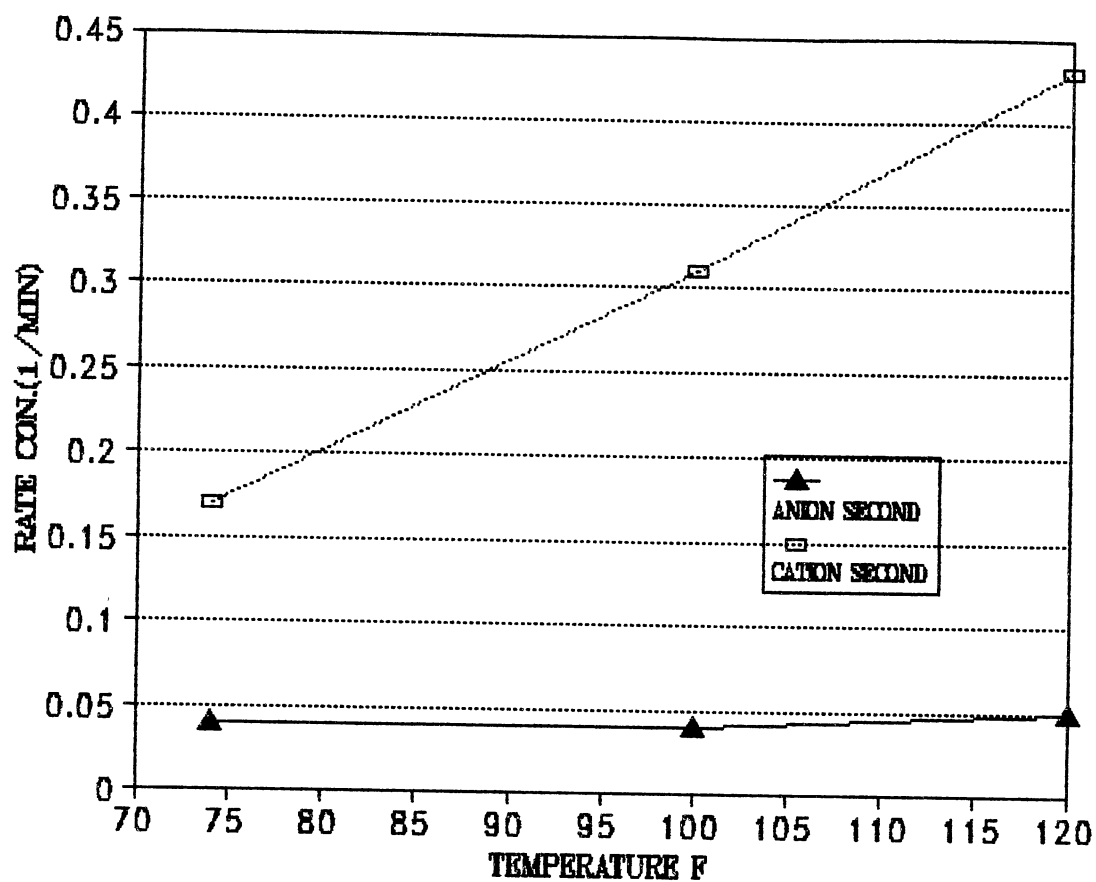


Figure 4. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 10% Water Using Cation Treatment For Anion Treated Solution And Anion treatment For Cation Treated Solution

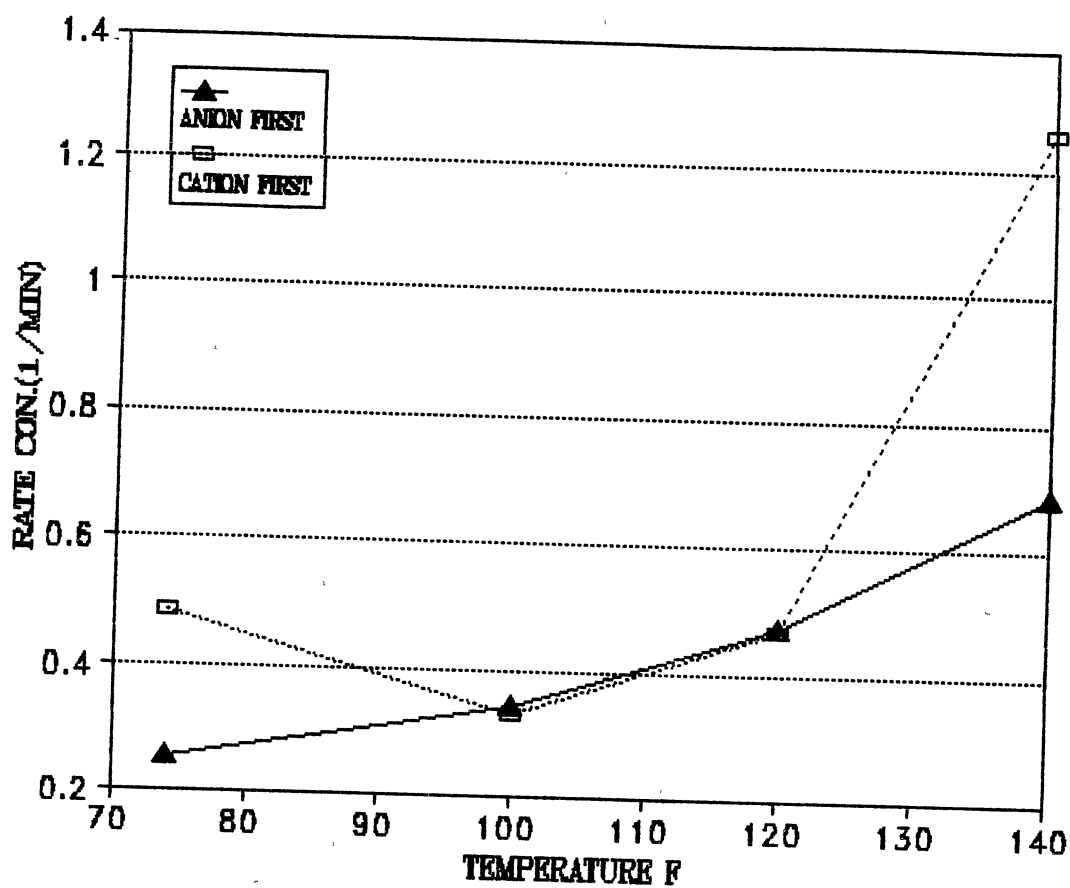


Figure 5. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 20% Water Using Cation Treatment First And Anion Treatment First

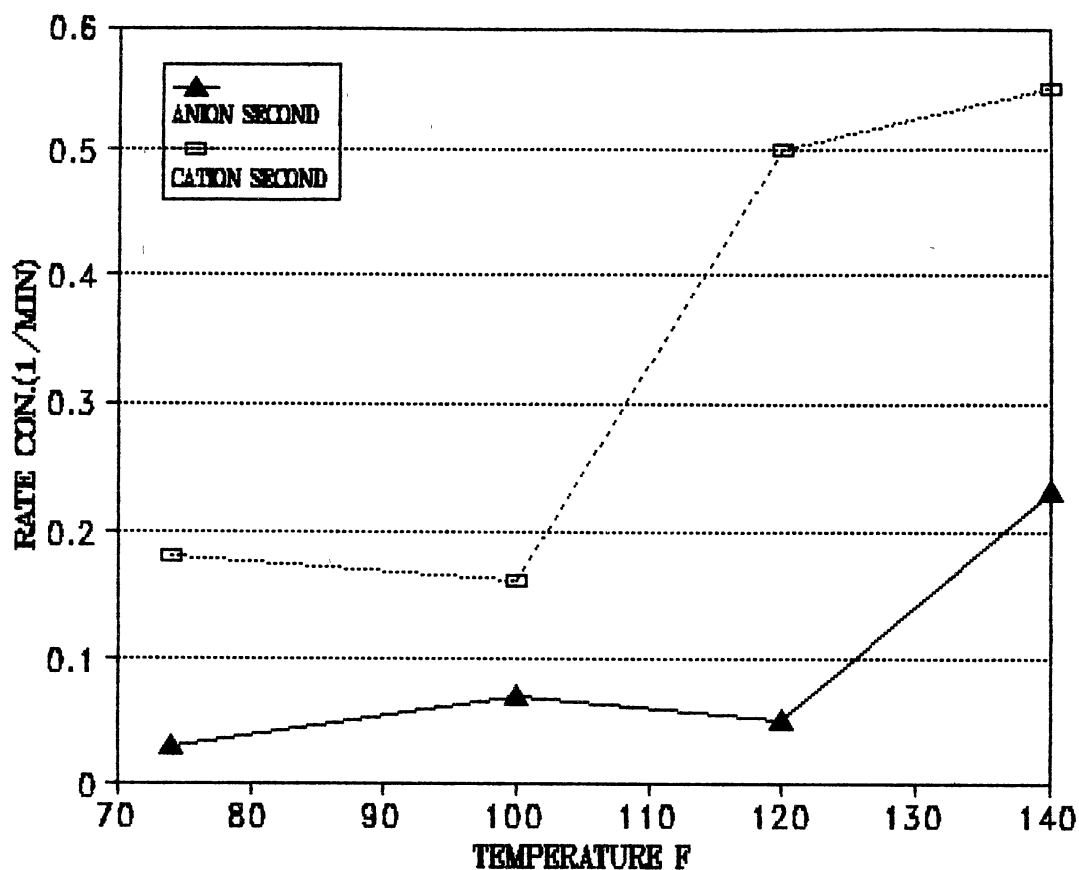


Figure 6. Comparison Of The Effect Of Temperature On Rate Constants For Batch Experiments For TEG With 20% Water Using Cation Treatment For Anion Treated Solution And Anion Treatment For Cation Treated Solution

solution. Figure 7 shows higher lag times for anion treatment followed by cation treatment than cation treatment followed by anion treatment. A gradual decrease in lag time with temperature can also be seen for both type of resins and water contents.

Figure 8 shows that for anion treatment followed by cation treatment with 10% water TEG there is no significant effect on chloride removal with temperature. This is shown by the experimental error bars (Table 26 in Appendix A). Calculations of experimental error bars are shown in Appendix D.

Figure 9 shows that cation treatment followed by anion treatment with 10% water TEG has a substantial decrease in chloride removal with temperature.

Figure 10 shows that anion treatment followed by cation treatment with 20% water TEG has little effect on chloride removal with temperature. This is shown by the experimental error bars.

Figure 11 shows that cation treatment followed by anion treatment with 20% water TEG has no effect on chloride removal with temperature.

Based on these batch experiment results, column experiments were carried out without water and with 15% water, and the data is presented in Tables 27 and 28, respectively (Appendix A). Breakthrough curves are generated by plotting chloride concentration versus time (Figure 12). A small peak was observed initially. This might be due to channeling of TEG in the column. In the

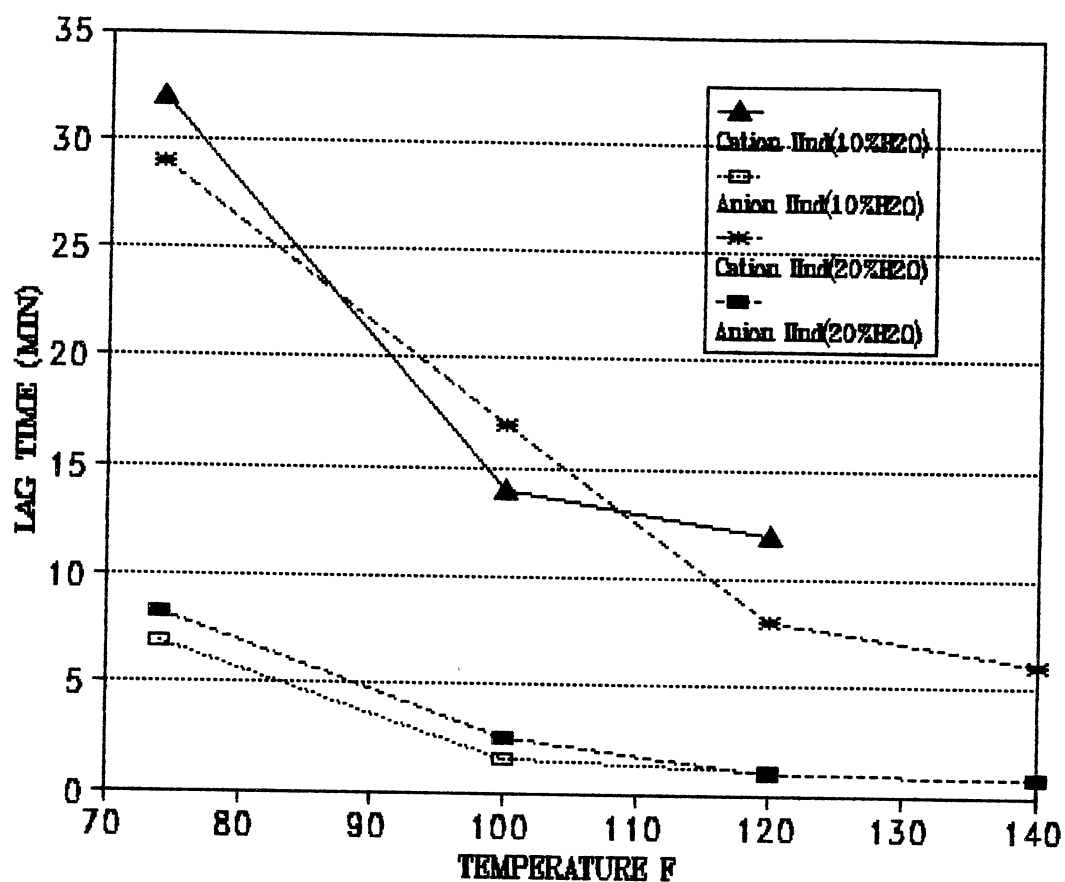


Figure 7. Effect Of Temperature On Lag Times For Batch Experiments For TEG With 10% And 20% Water Using Cation Treatment For Anion Treated Solution And Anion Treatment For Cation Treated Solution

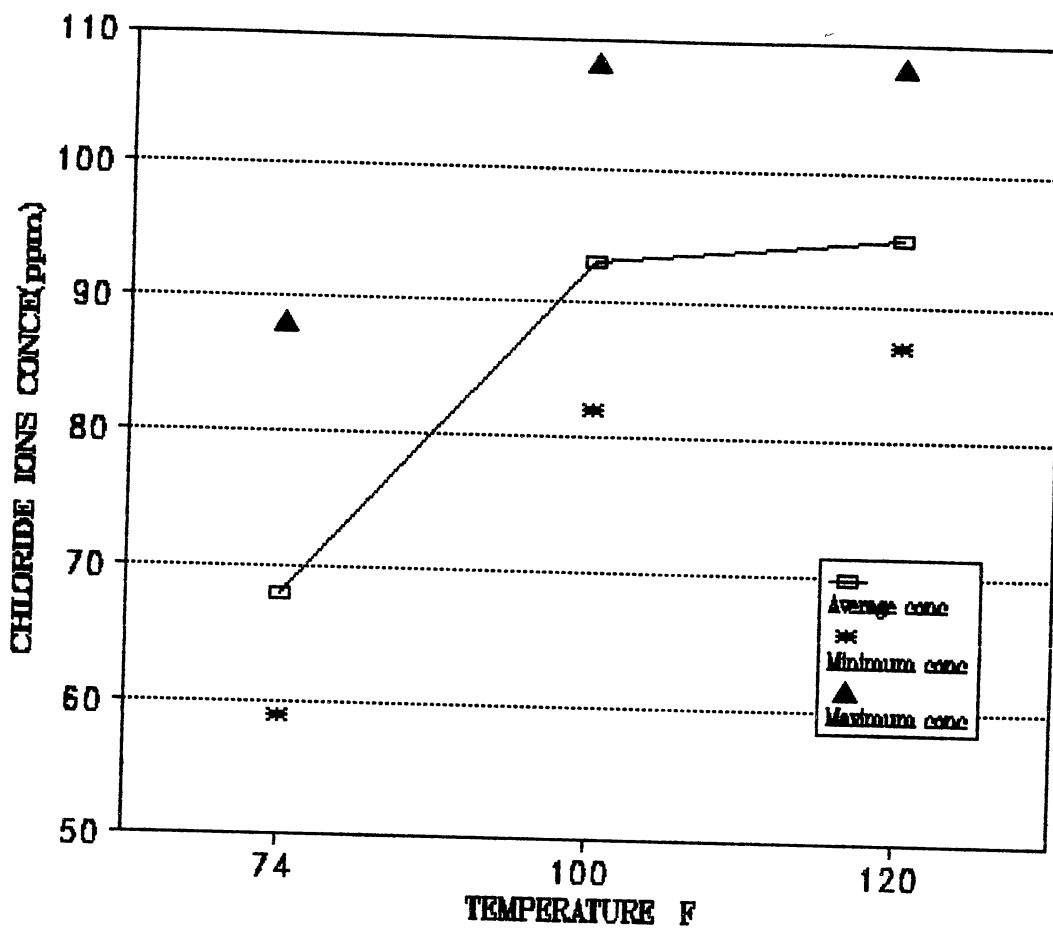


Figure 8. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 10% Water Using Anion Treatment First

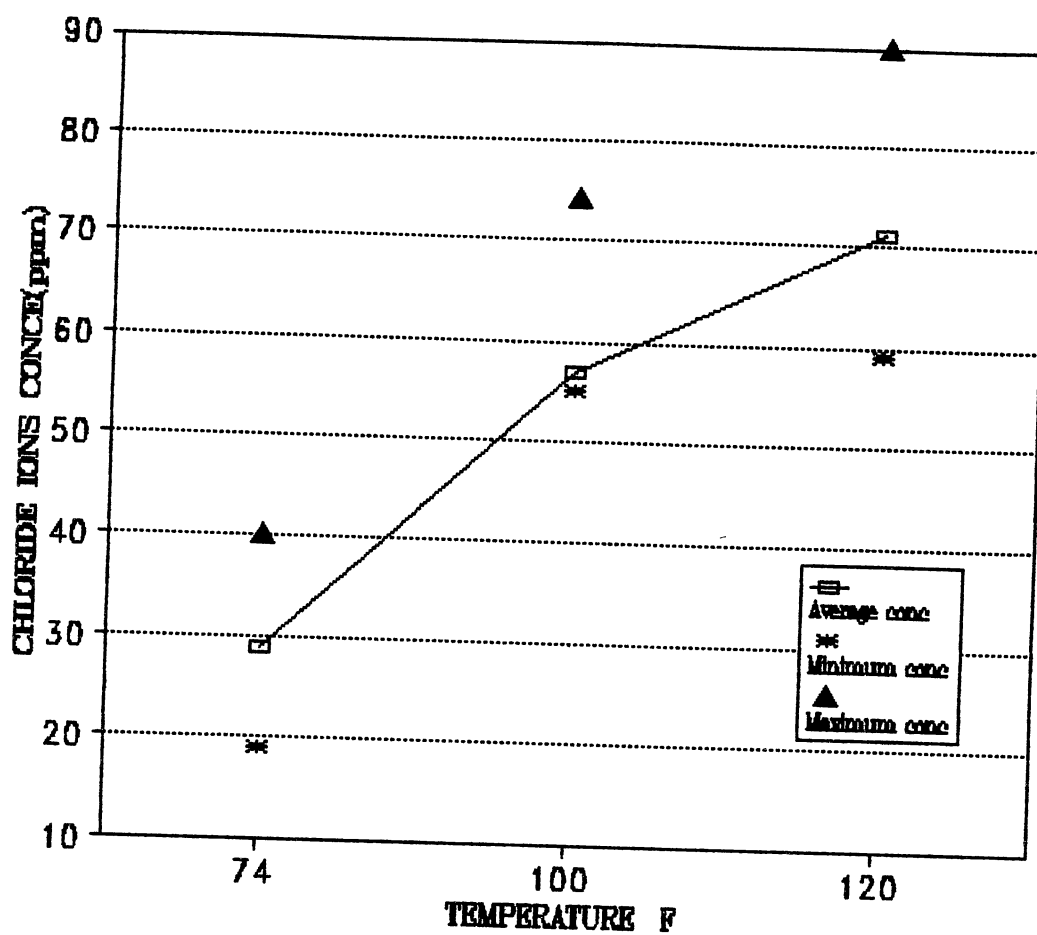


Figure 9. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 10% Water Using Cation Treatment First

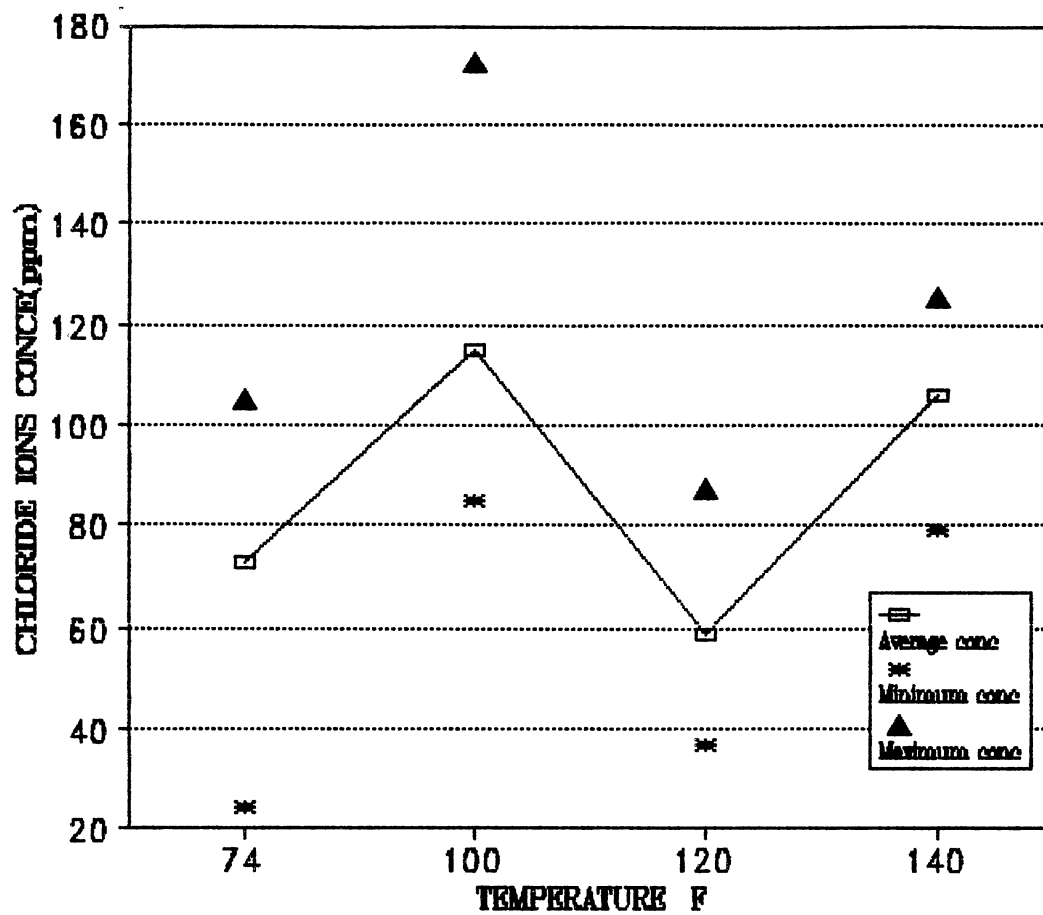


Figure 10. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 20% Water Using Anion Treatment First

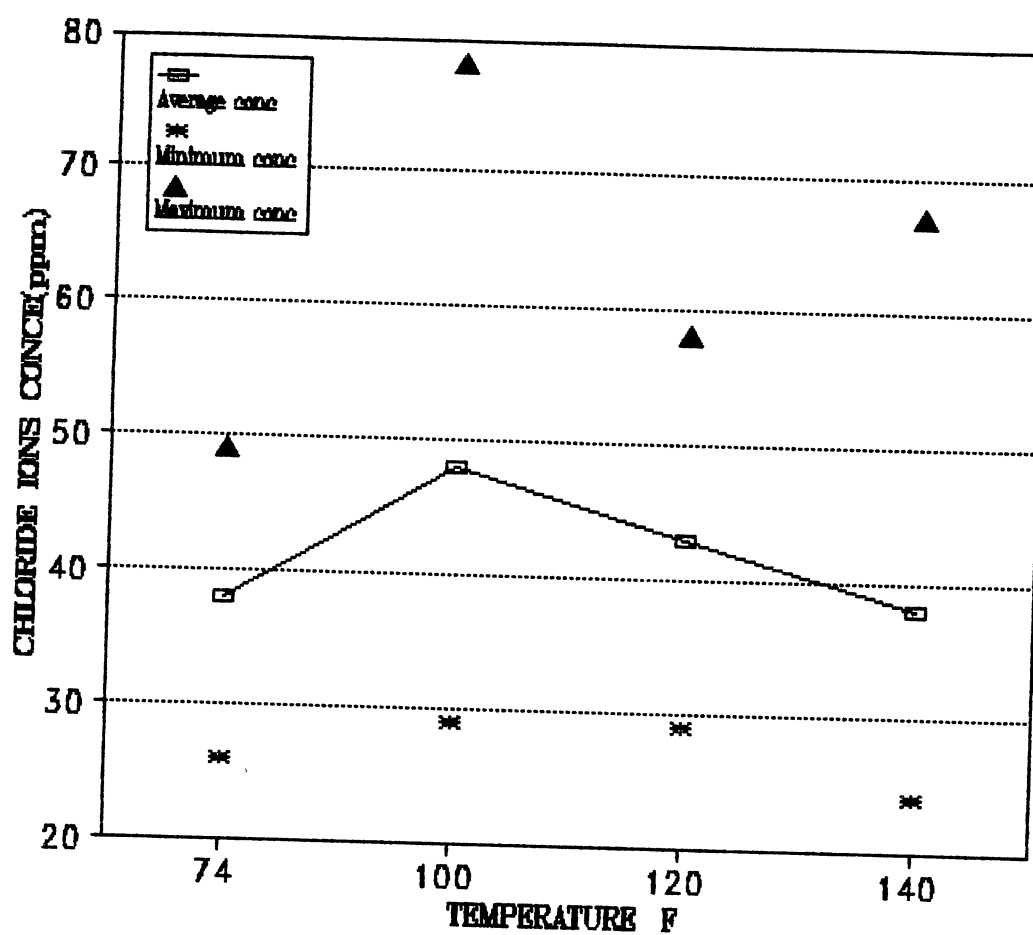


Figure 11. Experimental Error Bars And The Effect Of Temperature On The Removal Of Chloride Ions For Batch Experiments For TEG With 20% Water Using Cation Treatment First

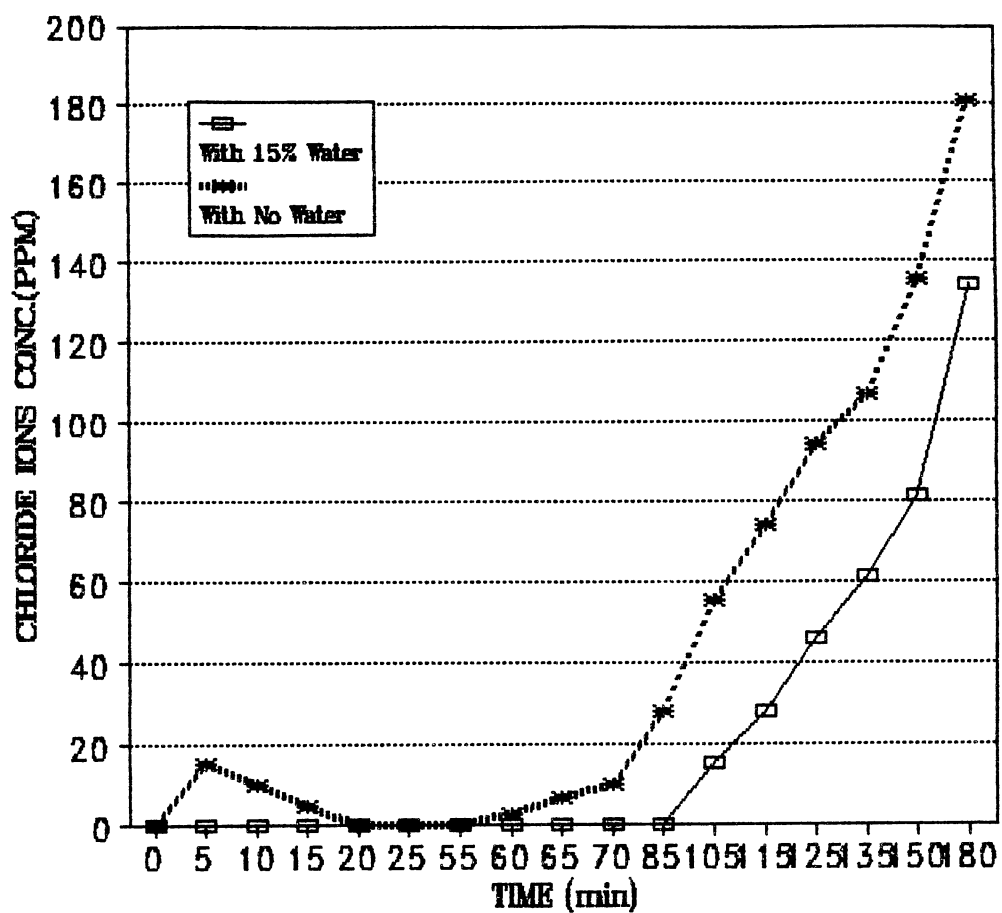


Figure 12. Breakthrough Curves For Column Experiments For TEG Without Water And With 15% Water Using Cation Treatment Followed By Anion Treatment

column run, the lag time was not observed as in the batch experiments.

To study the lag time six batch experiments were conducted using wet resin, dry resin, and resin soaked in TEG solution (Table 30, Appendix A). Plots were made for pH change with time for these experiments. For cation treatment first, lag time was not observed (Fig 13). For anion treatment of cation treated solution lag time was observed (Fig 14). Also, Figure 14 shows that the pore size and the shielding effect of water on the resin particles are not prominent.

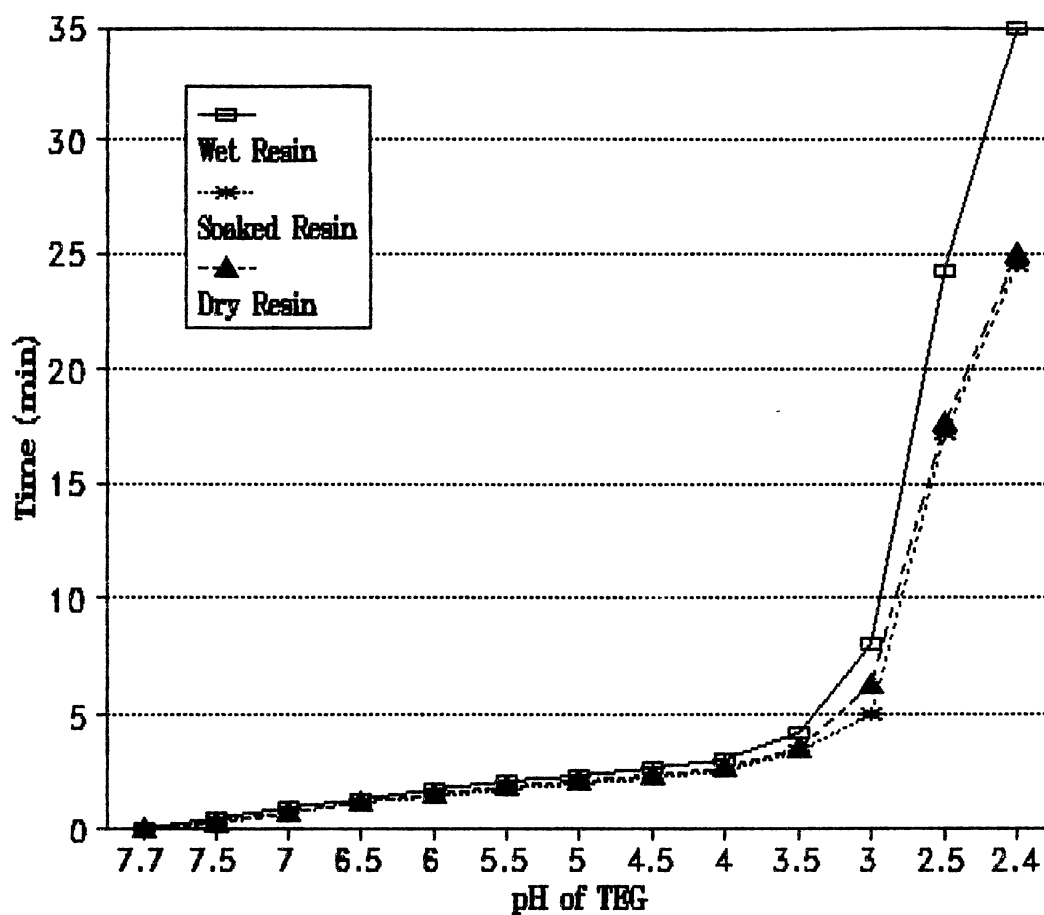


Figure 13. Time Versus pH Change For Batch Experiments For TEG With 20% Water At Room Temperature Using Wet, Dry, And Resins Soaked In Pure TEG With Cationic Treatment First

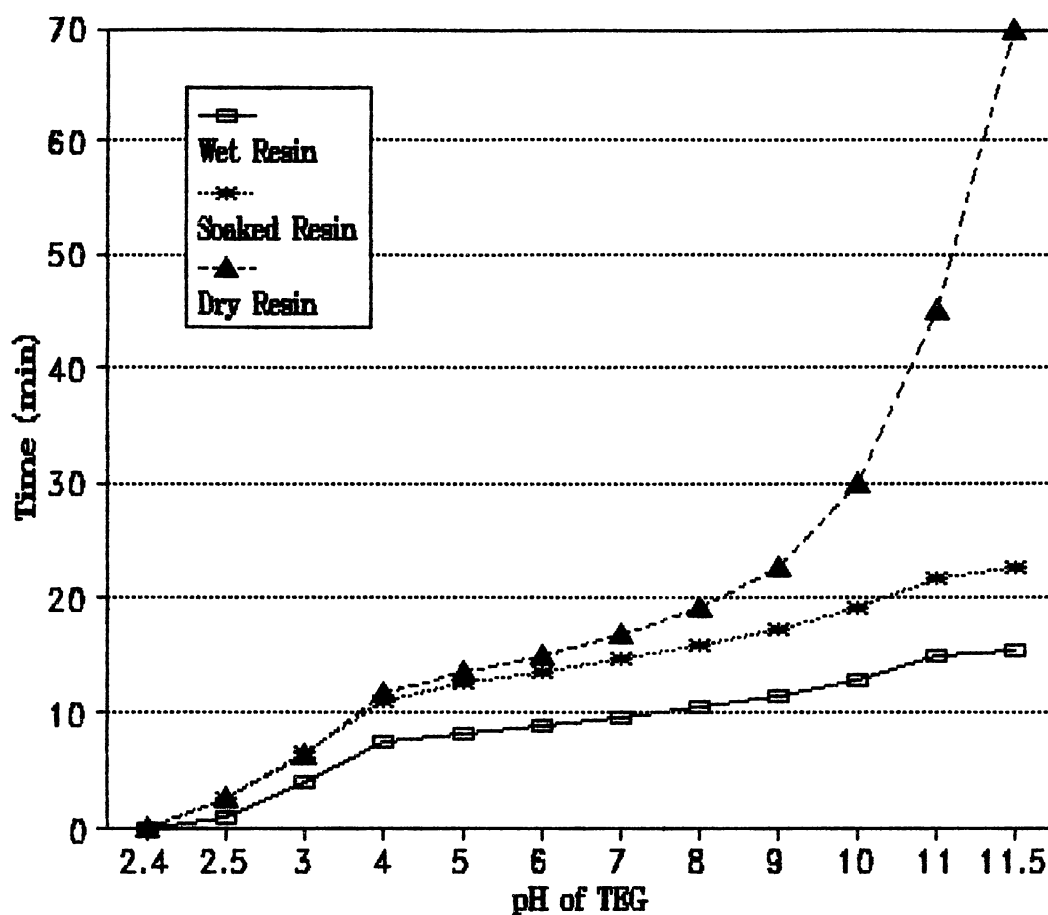


Figure 14. Time Versus pH Change For Batch Experiments For TEG With 20% Water At Room Temperature Using Wet, Dry, And Resins Soaked In Pure TEG with Anionic Treatment For Cation Treated Solution

CHAPTER V

PROCESS DESIGN AND COST ESTIMATION

Ion-exchange processes are proposed for the desalting of TEG. The purification loop has a charcoal filter and an ion-exchange filter and treats 30 gpm of the 300 gpm TEG throughput on a continuous basis. The charcoal filter removes the organic impurities, and ion-exchange facility will significantly reduce the chloride, sodium, magnesium, and calcium ions which tend to accumulate in the glycol.

The process design and economic evaluation is done based on References 10-17. An overall flow diagram for the desalting of TEG, including the charcoal filter, is given in Figure 15. Valves v1, v2, v3, and v4 control flow of TEG in and out of the desalting loop, pH meters M1 and M2 measure the TEG pH in and out of the loop. Valves v1 and v4 remain open at all times while the purification is in use. When pH at M2 begins to drop below 8.8 (pH of TEG with 25/ppm of Cl was measured as approximately 8.8), the operation should be stopped (opening v3 and closing v2), and resin should be regenerated or replaced with fresh resin. The resin may be effective for approximately 5-6 months for initial operation. Its effective operation after the regeneration will be known only after the system is placed in operation.

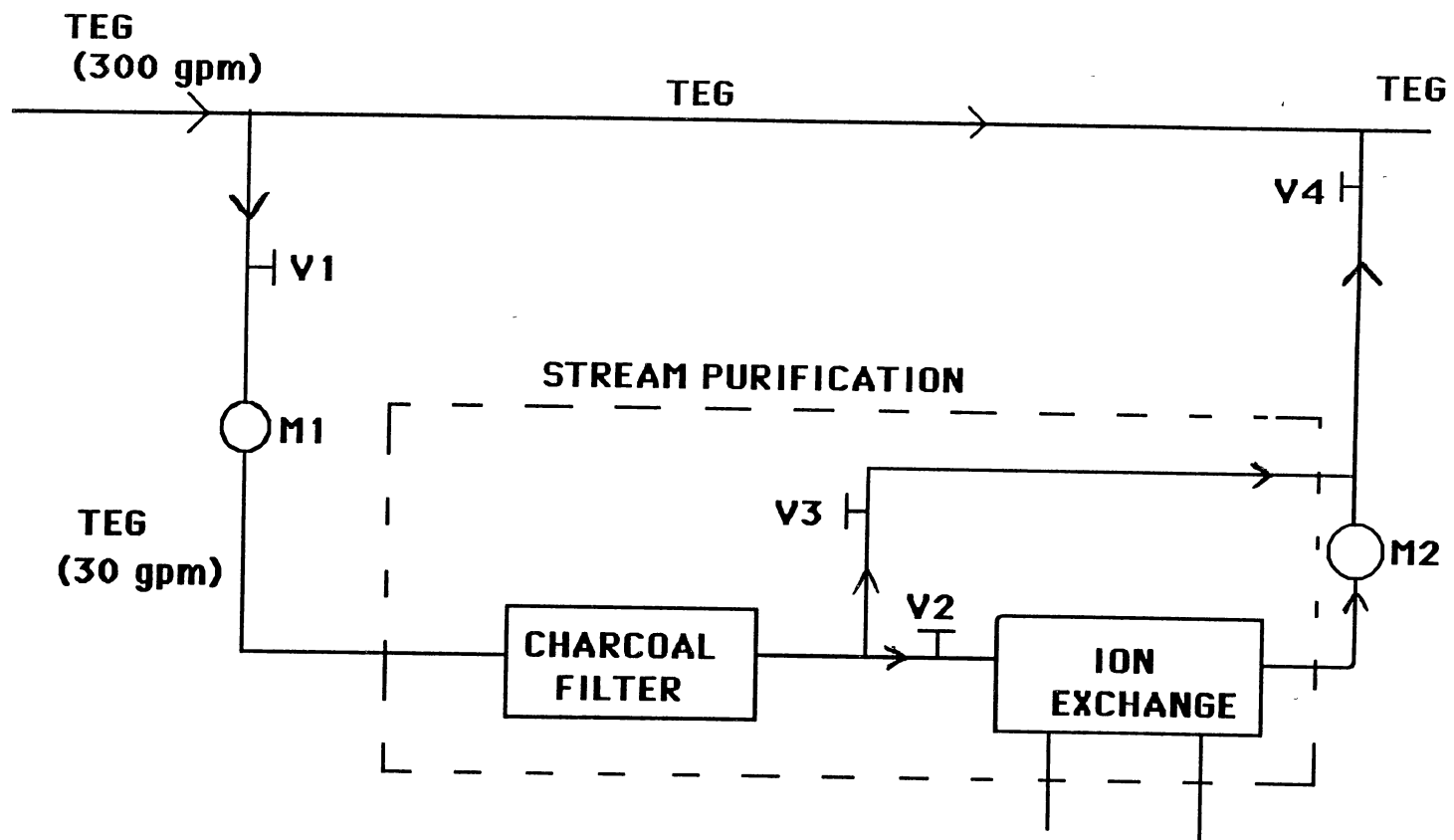


Figure 15. Flow Chart For TEG Stream Purification

The ion exchange process for purification of TEG is considered for three scenarios

- (i) operation at 180⁰F with regeneration,
- (ii) operation at 180⁰F and contracting out for regeneration,
- (iii) operation at 220⁰F (i.e. at process stream entrance temperature) without regeneration.

A plant layout for the ion-exchange process at 180⁰F with regeneration is given in Figure 16. It consists of a heat exchanger (double pipe), placed next to the charcoal filter, two ion-exchange columns, cationic column first and anionic column second. For the second case, i.e. operation at 180⁰F and contracting out for regeneration, the regeneration will be done outside the plant. For the third case, ion exchange process at 220⁰F, heat exchanger will not be present. The plant layout for this process is shown in Figure 17.

The TEG, after passing through the charcoal filter, is cooled from 220⁰F to 180⁰F using a double pipe heat exchanger, with water as the cooling medium. The TEG then enters the top of the cation exchanger column. The residence time in this unit will be about 2 minutes, where cations (sodium, magnesium, and calcium) are removed. The TEG stream then enters the top of the anion exchange column where anions (chlorides) are removed. The residence time will be about 2 minutes. The order of the resin used and residence time for both the columns are based on the batch and column experimental results.

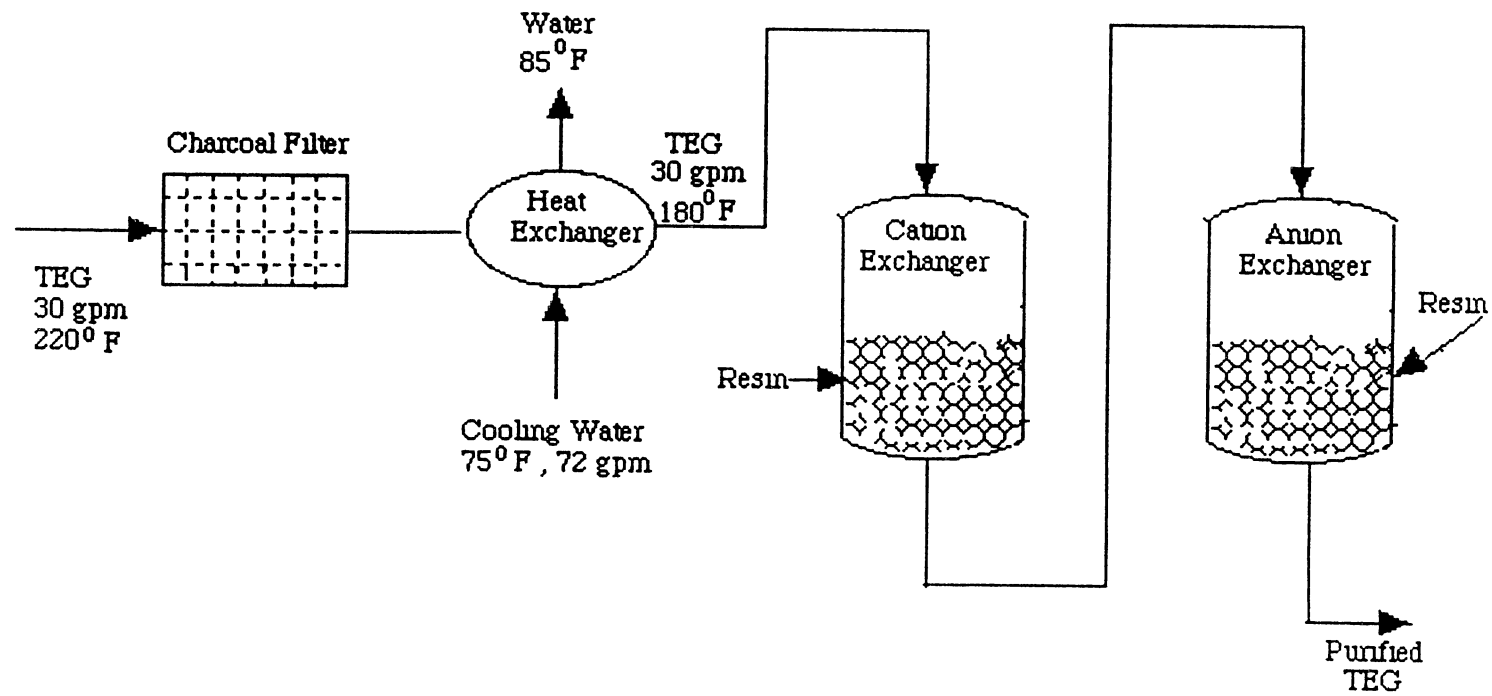


Figure 16. Plant Layout For Ion-Exchange Process
At 180°F

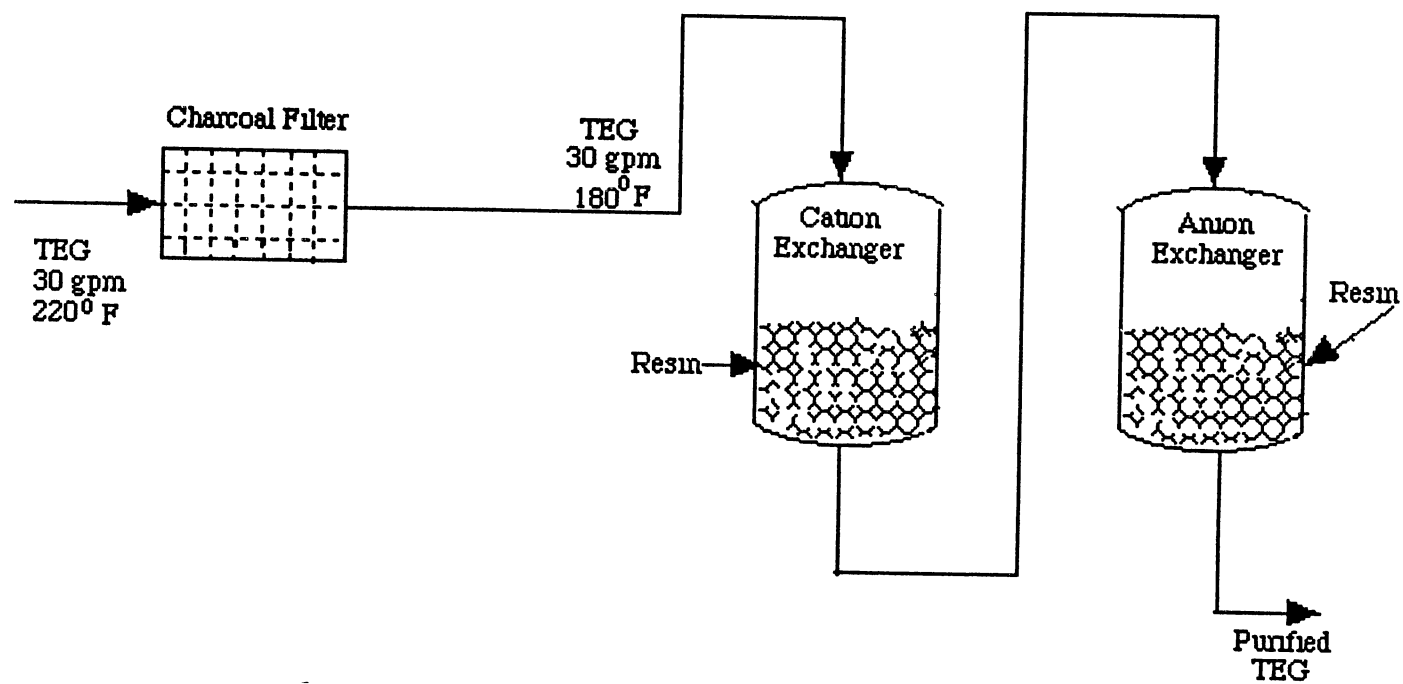


Figure 17. Plant Layout For Ion-Exchange Process
At 220°F

During the regeneration process, the regenerants, 8% sulfuric acid and 4% Sodium hydroxide, are pumped into the cation and anion exchange columns, respectively, from drums brought to the site. This regeneration is continued until no more sodium, calcium, and magnesium ions can be detected in the cation exchanger regenerant and no more chloride ions in the anion exchanger regenerant.

In the second process, the TEG is circulated through the purification loop, till the resin capacity is exhausted (detector M2). The ion-exchange process is then stopped for replacement of the resin, and the used resin is sent to a contractor for regeneration.

In the third proposed process, the TEG stream enters the cation exchange column directly, at 220⁰F, from the charcoal filter. At this high temperature, the anionic ion-exchange resin will not last long due thermal degredation of the resins. The used resins at this temperature are not suitable for the regeneration, and are to be incinerated and fresh resin is installed. At 220⁰F the fresh resin works well for one time use(19).

Equipment Sizing and Materials

This section will present the procedures used to size columns, and heat exchangers to be used in the proposed design. An estimate of the amount of ion exchange resin required and the regenerants for regeneration will also be given.

(i) Cation Exchange Column:

The size of this column was based on the volumetric flow rate of TEG (30 gpm) and on estimated residence time at the operating temperature from preliminary experiments. The batch experiments showed little or no effect with temperature and addition of water. So the residence time of C_T140_W20(FIRST), about two minutes, is assumed for the process at 180°F. Volume of the column was double the volume required by the above constraints to ensure enough room was provided for the resin swelling and for the flow of TEG.

A resin porosity of 40% was assumed for the column, and the residence time was estimated as two minutes. A maximum of 3 ft bed height was assumed in calculating the diameter and the length of the column, and are within the design limits.

(ii) Anion Exchange Column:

Sizing of the anion exchange column is similar to that of cation exchange column. For this, the column experimental results were used to find the residence time for the column. A residence time of two minutes was calculated for the anion exchange column. Characteristics of these columns are given in Table 1.

TABLE 1
CHARACTERISTICS OF ION EXCHANGE COLUMNS

Residence		Bed		Vol	
Time	Diameter	Height	Depth	Flow	Fraction
(min)	(ft)	(ft)	(in)	(gpm/ft ²)	Resin
Cat. Ex.	2.0	3.0	6.0	36	4.24
An. Ex.	2.0	3.0	6.0	36	4.24

(iii) Regenerant Requirements:

The amount of acid regenerate (sulfuric acid) required for an initial regeneration was estimated as 1.25 times the void volume of the resin bed. This volume is estimated to be about 10 ft³.

Similarly the volume of the Caustic regenerate (NaOH) was estimated to be about 10 ft³.

(v) Resin Requirements:

The ion exchange resins are of central importance in the ion exchange process. This design is based on the use of Rohm and Hass Amberlyst A-15 and A-21. These resins were used in the preliminary batch experiments and column experiments for the determination of residence time for the anion and cation exchange columns. For the present design, the volume of cation and anion resins are about 20 ft³ each.

(vi) Heat Exchanger:

A heat exchanger will be placed immediately after the charcoal filter in the process stream to reduce the temperature of TEG from 220⁰F to 180⁰F, using cooling water. A double pipe counter flow exchanger is chosen for this purpose. The solvent heat capacity, density and viscosity are given in Appendix D. Cooling water at 75⁰F will be used in the heat exchanger and the hot water temperature was set at 85⁰F, which gave a water flow rate of 72 gpm.

Choosing a NPS one and half inch ID schedule 40 steel pipe for the inner tube, the solvent Reynolds number is calculated and found to be in turbulent flow. So an overall heat transfer coefficient is estimated as

$$U_o = 75 \text{ btu/hr ft}^2 \text{ F.}$$

Using standard procedures, the area required for the heat exchanger was calculated to be 40.7 ft², which gave a length of pipe required of about 102 ft (i.e 5x20ft). and the pressure drop is calculated of about 2.75 psi, which is within the acceptable range. A four inch O.D. schedule 40 carbon steel pipe is chosen for the water side.

(vii) Pumps:

Two 1 HP centrifugal pumps will be necessary to pump the acid (sulfuric acid) and caustic (sodium hydroxide).

Cost Estimation

A detailed cost estimation is done for the three scenarios. The costs for equipment and materials for use in the plant expansion were estimated from available sources (13, 14, 15). To update the cost, plant indices are used (M and S equipment cost index).

Frequency of regeneration or incineration of the resin plays a major role in the total plant cost. The frequency of regeneration for the process is determined, by assuming an overall 100 ppm of NaCl per year, since about 825 ppm of salts accumulated in the TEG solution over the last eight years. The glycol dehydration unit (GDU) has a glycol volume of 48,000 gal. So the ideal regeneration time, i.e., the utilization of total resin capacity, was estimated about 29 months. But the column experimental breakthrough curve gave about 16% utilization of resin. So the frequency of regeneration is estimated as about 5 months.

The cost estimations for the proposed ion-exchange process are given in Tables 2, 3, and 4. The comparative fixed capital costs and operating costs are listed in Table 5.

TABLE 2
COST ESTIMATION FOR ION-EXCHANGE PROCESS AT 180°F
WITH REGENERATION UNIT

Fixed Capital Cost	
Equipment Cost	

Description	Cost (US \$)

Cation Exchange Column	9000
Anion Exchange Column	9000
Heat Exchanger (Double pipe)	6000
Acid Tank (Two 55gal HDPE Tanks)	330
Caustic Tank (Two 55gal HDPE Tanks)	330
Two Pumps	2000
Total Equipment Cost (E)	26,600
Scale up factors	
(i) Equipment erection 40% of E	0.4 E
(ii) Piping 30% of E	0.3 E
(iii) Instrumentation 30% of E	0.3 E
(iv) Utilities 20% of E	0.2 E
(v) Storage (for used acids and caustics) 5% of E	0.05E

Total Scale up Factors Cost	1.25E
Fixed Capital Costs = (\$ 26,600) (1 + 1.25)	
= 60,000	

Table 2 (continued)

Operating Costs	
Yearly Basis	

Description	Cost (US \$)

1. Cation Exchange Resin	3,000
2. Anion Exchange Resin	3,000
3. Acid Regenerant (3 regenerations)	200
4. Caustic Regenerant (3 regenerations)	200
5. Maintenance (10% FCC)	6,000
6. Miscellaneous Supplies (10% of Mainten.)	600
7. Utilities (power etc.)	600
8. Water (75gpm @ 0.05/1000 gal)	2,000
9. Operating Labor	10,000
10. Supervision (20% of 9)	2,000
11. Laboratory Costs (25% of 9)	2,500
12. Plant Overheads (50% of 9)	5,000
13. Capital Charges (15% of FCC)	9,000
14. Rates (2% of FCC)	1,200
Total Operating Costs	46,000

TABLE 3
ECONOMIC EVALUATION FOR ION-EXCHANGE PROCESS AT 180°F
AND CONTRACTING OUT FOR REGENERATION

Fixed Capital Cost	
Equipment Cost	

Description	Cost (US \$)

Cation Exchange Column	9000
Anion Exchange Column	9000
Heat Exchanger (Double pipe)	6000

Total Equipment Cost (E)	24,000

Scale up factors	
(i) Equipment erection 40% of E	0.4 E
(ii) Piping 30% of E	0.3 E
(iii) Instrumentation	0.3 E
(vi) Utilities 20% of E	0.2 E
(v) Storage(used resin etc.) 5% of E	0.05E

Total Scale up Factors	1.25E
Fixed Capital Costs = (\$ 24,000) (1 + 1.25)	
= 54,000	

Table 3 (continued)

Operating Costs

Yearly Basis

Description	Cost (US \$)
1. Cation Exchange Resin (40 ft ³ @ \$150/ft ³)	6,000
2. Anion Exchange Resin (")	6,000
3. Regeneration Costs (contract @ \$75/ft ³)	9,000
4. Maintenance (10% FCC)	5,400
5. Miscellaneous Supplies (10% of Mainten.)	600
6. Utilities (power etc.)	600
7. Water (75gpm @ 0.05/1000 gal)	2,000
8. Operating Labor	9,000
9. Supervision (20% of 8)	1,800
10. Laboratory Costs (25% of 8)	2,250
11. Plant Overheads (50% of 8)	4,500
12. Capital Charges (15% of FCC)	8,100
13. Rates (2% of FCC)	1,080
Total Operating Costs	57,000

TABLE 4
ECONOMIC EVALUATION FOR ION-EXCHANGE PROCESS AT 220°F
WITH INCINERATION OF RESIN EACH TIME

Fixed Capital Cost	
Equipment Cost	

Description	Cost (US \$)

Cation Exchange Column	9000
Anion Exchange Column	9000

Total Equipment Cost (E)	18,000

Scale up factors	
(i) Equipment erection 40% of E	0.4 E
(ii) Piping 30% of E	0.3 E
(iii) Instrumentation	0.3 E
(vi) Utilities 20% of E	0.2 E
(vii) Storage(used resin etc.) 5% of E	0.05E

Total Scale up Factors	1.25E
Fixed Capital Costs = (\$ 18,000) (1 + 1.25)	
= 41,000	

Table 4 (continued)

Operating Costs	
Yearly Basis	

Description	Cost (US \$)

1. Cation Exchange Resin (60 ft ³ @ \$150/ft ³)	9,000
2. Anion Exchange Resin (")	9,000
3. Incineration Costs (incineration @ \$90/ft ³)	11,000
4. Maintenance (10% FCC)	4,100
5. Miscellaneous Supplies (10% of Mainten.)	500
6. Utilities (power etc.)	500
7. Operating Labor	8,000
8. Supervision (20% of 7)	1,600
9. Laboratory Costs (25% of 7)	2,000
10. Plant Overheads (50% of 7)	4,000
11. Capital Charges (15% of FCC)	6,000
12. Rates (2% of FCC)	800
Total Operating Costs	57,000

TABLE 5
COMPARITIVE COST ESTIMATION FOR ION-EXCHANGE PROCESSES

Description	Fixed capital cost	operating Cost
1) Process at 180 ⁰ F with with regeneration	\$60,000	\$48,000
2) Process at 180 ⁰ F with contracting out for regeneration	\$54,000	\$57,000
3) Process at 220 ⁰ F without regeneration	\$41,000	\$57,000

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

(1) An ion-exchange unit to purify a TEG stream has been designed based on lab scale batch and column experiments. This unit is expected to reduce the chloride ion concentration from 825/ppm to less than 25/ppm and significantly reduce other ionic impurities, and thus, decreasing the corrosion and fouling effects in the process equipment.

(2) From the batch and column experiment results it is seen that the temperature and addition of water have very little effect on the removal of ionic impurities for cationic treatment followed by anionic treatment. Also decreased for anionic treatment followed cationic treatment. The cationic treatment first gave better results than anionic treatment first. This might be due to the type of resin used.

(3) Lag time was observed when the second resin is used for the TEG treatment in batch experiments and the lag time was more for cation second than anion second. This lag time was not seen in the column experiments. From the lag time experiments it is seen that the absence of water layer on the resin particles and soaking the resin in pure in TEG did not showed any effect on lag time. So the

absence of lag time in column experiments may not be due to fluid displacement, but could be enhanced diffusion.

(4) In the ion-exchange process the cation exchange column should be followed by anion exchange column. Approximate residence times for the cation and anion exchange columns are obtained from laboratory experiments. The residence times for both anion and cation exchangers are about 2 min.

(5) The resins used in the laboratory work, Rohm and Hass Amberlyst 15 and 21 gave consistent results, and the design of the plant is based on the characteristics of these resins.

(6) A counter-current regeneration technique should be used with the present design for Process 1. This will eliminate the coagulation of resin particles. Also countercurrent regeneration will be more effective, since the ionic impurities congregate at the bottom of the resin bed.

(7) The cost evaluation indicates that the operating costs for all the three proposed process are approximately the same.

Recommendations

(1) A glycol stream purification loop for the removal of ionic impurities should be placed in the existing purification loop containing the charcoal filter. This will significantly reduce the corrosion and fouling problems in the process equipment, also will ensure continuous operation.

(2) The ion-exchange process at 180°F with contracting out for regeneration is recommended for the scale up plant.

(3) Data collected during operation of the system can subsequently be used to fine tune the system operating parameters.

BIBLIOGRAPHY

1. Gritsenko, A.I., Budymka, V.F., and Vlasyuk, O.I.
" Use of Ion-Exchange Filters to remove Salts from Diethylene Glycol." Gazaq.Delo (USSR) 10 (1970).
2. Matvienko, V.G., Yarym-Agaev, N.L., and Cherkasskaya, V.V. " Removal of Salts from Diethylene Glycol." Otkrytiya, Izobret (USSR) 48, (1980).
3. Matvienko, V.G., and Yarym-Agaev, N.L. " Removal of Dissolved Salts from Glycol with Benzene." Prom-St (USSR) 1, (1988).
4. Martynek, M., Sebastinaka, S. and Gorczyca, J.
"Diethylene Glycol Desalting with Ion-Exchangers." Naftalkatowics (Poland) 28,12 (1972).
5. Monick, J.A., " Alcohols Their Chemistry Properties and Manufacture." Reinhold Book Corporation, New York (1968).
6. Lloyd, W.G., and Taylor, F.G. "Corrosion by and Deterioration of Glycol and Glycol Amine Solutions." Industrial and Engineering Chemistry 46, 11 (1957).
7. Angelo Chianese, Serigio Di Cave, and Barbara Mazzarotta. "Solubility and Metastable Zone width of Sodium Chloride in water-Diethylene Glycol Mixtures." Journal of Chemical Engineering Data 31, 3 (1986).
8. Giorgio, C., and Pigford, R.L. "Periodic Countercurrent Operation of Sorption Processes Applied to Water Desalination with Thermally Regenerable Ion-exchange Resins." Industrial Engineering Chemical Fundamentals 25, 4 (1986).
9. Black, Sivalls, and Bryson Inc. "High Concentration Glycol Dehydration." Hydrocarbon Processing (International Edition) 65, (1986).
10. Dean, J.A. Handbook of Organic Chemistry. McGraw-Hill book Company, New York (1987).
11. Chen, N.H. Process Reactor Design. Allyn and Bacon Inc. Boston, 1983.
12. Levenspiel, O. Chemical Reaction Engineering. Wiley Eastren Limited, Hyderabad, India. IInd ed (1972).

13. Sinnott, R.K. Chemical Engineering Vol 6. Pergamon Press, New York (1986).
- ✓ 14. Peters, M.S., and Timmerhaus, K.D. Plant Design and Economics for Chemical Engineers. McGraw-Hill Book Company second ed.(1968).
- ✓ 15. Chemical Engineering . "Chemical Engineering Plant Cost Index" Chem.Eng. 96, 3rd Quarter (1989).
16. Perry, R.H., and Chilton, C.H. Chemical Engineers Hand Book. McGraw-Hill book company 5th ed. New York (1972).
17. Bell, K.J. "Process Heat Transfer", Class notes, CHENG 5423, OKLAHOMA STATE UNIVERSITY, Spring (1990).
18. Fisher 88 , Fisher Catalogue; (1988).
19. Robert Kunin. Ion Exchange Resins John Wiley & Sons Inc. 2nd edition New York (1958).
20. Young, M.A. "Preliminary Design & Cost Analysis for a Tetraethylene Glycol Stream Purification Process." Doctoral Report. Oklahoma State University, Stillwater, OK. (1990).
21. Zecchini, E.J. and King, D.W. Private Communications, Oklahoma State University, Stillwater, OK. (1990).

APPENDIX A
EXPERIMENTAL DATA

TABLE 6

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 74F FOR
TEG WITH 10% WATER USING ANION TREATMENT FIRST

RESIN USED	min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6.8	7.91	0
	1	1	8.3	9.32	1
	2	0	8.9	9.9	2
	3	46	9.6	10.5	3.8
	5	58	11.2	12	6
	6	49	11.9	12.7	6.8
	8	37	12.4	13.2	8.6
	9	12	12.5	13.3	9.2
	10	0	12.6	13.4	10
	12	20	12.8	13.6	12.3
	14	10	12.9	13.7	14.2
	16	30	13	13.7	16.5
	20	0	13.1	13.8	20
	26	45	13.2	13.9	26.8
	42	30	13.3	14	42.5
EQUILIBRIUM	60	0	13.3	14	60
CATIONIC RESIN	0	0	13.25	14	0
	6	30	13.1	13.8	6.5
	10	25	13	13.7	10.4
	15	40	12.9	13.6	15.7
	18	45	12.8	13.5	18.8
	21	10	12.7	13.4	21.2
	23	35	12.6	13.3	23.6
	30	0	12.2	13	30
	33	52	11.7	12.5	33.9
	35	58	11	11.9	36
	36	54	10.6	11.5	36.9
	38	51	9.9	10.8	38.9
	42	6	9.3	10.3	42.1
	46	42	8.7	9.7	46.7
	49	17	7.7	8.8	49.3
	52	33	6.3	7.4	52.6
	56	4	5	6.2	56.1
	59	10	3.6	4.9	59.2
	61	4	2.8	4.1	61.1
	68	45	2	3.4	68.8
	74	55	1.8	3.2	74.9
	81	0	1.7	3.1	81
	90	15	1.6	3	90.3
	110	0	1.5	2.9	110
EQUILIBRIUM	125	0	1.5	2.9	0

TABLE 7

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 74F FOR
TEG WITH 10% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6.65	7.8	0
	1	1	4	5.3	1.01
	2	4	1.8	3.2	2.06
	3	23	1.4	2.8	3.38
	4	45	1.2	2.6	4.75
	5	36	1.1	2.5	5.6
	7	56	0.9	2.4	7.93
	10	5	0.8	2.3	10.1
	16	20	0.6	2.1	16.3
	21	45	0.5	2	21.8
	30	15	0.4	1.9	30.3
	43	0	0.3	1.8	43
	65	0	0.2	1.7	65
EQUILIBRIUM	80	0	0.2	1.7	0
ANIONIC RESIN	0	0	0.2	1.7	0
	1	21	0.4	1.9	1.35
	2	12	0.5	2	2.2
	3	45	0.7	2.2	3.75
	4	28	0.8	2.3	4.47
	5	40	1	2.5	5.67
	6	15	1.1	2.6	6.25
	7	15	1.3	2.7	7.25
	8	2	1.5	2.9	8.03
	9	2	1.9	3.3	9.03
	10	1	3	4.3	10
	11	14	6	7.2	11.2
	12	18	8	9	12.3
	13	41	9	10	13.7
	14	7	9.2	10.2	14.1
	15	7	9.7	10.6	15.1
	16	12	10.5	11.4	16.2
	18	4	11.7	12.5	18.1
	20	7	12.1	12.9	20.1
	21	5	12.2	13	21.1
	22	25	12.3	13.1	22.4
	24	22	12.4	13.2	24.4
	27	5	12.5	13.3	27.1
	33	0	12.6	13.4	33
	50	0	12.7	13.5	50
EQUILIBRIUM	70	0	12.7	13.5	0

TABLE 8

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 74F FOR
TEG WITH 20% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6.5	7.6	0
	0	18	5.5	6.7	0.3
	0	26	5	6.2	0.43
	0	41	4	5.3	0.68
	0	53	3	4.3	0.88
	1	18	2	3.4	1.3
	1	35	1.8	3.2	1.6
	1	57	1.6	3	1.95
	2	38	1.4	2.8	2.63
	3	45	1.2	2.6	3.75
	5	33	1	2.5	5.55
	23	25	0.5	2	23.4
	36	30	0.4	1.9	36.5
	70	0	0.3	1.8	70
EQUILIBRIUM	90	0	0.3	1.8	0
ANIONIC RESIN	0	0	0.3	1.8	0
	1	20	0.6	2.1	1.33
	3	25	0.9	2.4	3.41
	5	35	1.3	2.7	5.6
	6	5	1.4	2.8	6.1
	7	50	1.8	3.2	7.83
	8	58	2.2	3.6	9
	9	30	2.5	3.9	9.5
	10	0	3	4.3	10
	10	44	4.5	5.7	10.7
	11	54	6.5	7.6	11.9
	12	52	8	9	12.9
	13	23	8.5	9.5	13.4
	14	38	9.2	10.2	14.6
	15	20	9.5	10.5	15.3
	16	57	10.5	11.4	17
	17	43	11	11.9	17.7
	27	5	12	12.8	27.1
	33	30	12.1	12.9	33.5
	51	30	12.2	13	51.5
EQUILIBRIUM	70	0	12.2	13	0

TABLE 9

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 74F FOR
TEG WITH 20% WATER USING ANION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6.5	7.6	0
	0	30	8	9	0.5
	1	43	9	10	1.7
	3	1	10	10.9	3
	3	47	11	11.9	3.8
	5	3	12	12.8	5.1
	7	42	12.5	13.3	7.7
	9	17	12.6	13.4	9.3
	11	10	12.7	13.5	11.2
	14	54	12.8	13.6	14.9
	23	0	12.9	13.7	23
	60	0	13	13.75	60
EQUILIBRIUM	90	0	13	13.75	0
CATIONIC RESIN	0	0	13	13.7	0
	17	50	12.5	13.3	17
	27	18	12	12.8	27.3
	31	48	11.5	12.3	31.8
	33	49	11	11.9	33
	36	34	10.5	11.4	36.6
	39	15	10	10.9	39.3
	42	30	9.5	10.5	42.5
	43	4	9	10	43.1
	45	9	8.5	9.5	45.2
	47	13	8	9	47.2
	48	48	7.5	8.6	48.8
	50	3	7	8.1	50.1
	51	2	6.5	7.6	51
	53	10	6	7.2	53.2
	57	27	5.5	6.7	57.5
	60	13	5	6.2	60.2
	63	55	4	5.3	63.9
	65	24	3.5	4.8	65.4
	67	13	3	4.3	67.2
	71	15	2.5	3.9	71.3
	87	40	2	3.4	87.7
	98	30	1.9	3.3	98.5
	120	0	1.8	3.2	120
EQUILIBRIUM	135	0	1.8	3.2	0

TABLE 10

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 100F FOR
TEG WITH 10% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6.2	7.3	0
	0	15	5	6.2	0 25
	0	21	4.5	5.7	0.35
	0	27	4	5.3	0 45
	0	32	3.5	4 8	0.53
	0	37	3	4.3	0 62
	0	41	2 5	3.9	0.68
	0	45	2	3.4	0.75
	0	55	1 5	2.9	0.92
	1	27	1	2.5	1.5
	3	12	0.5	2	3.2
	6	20	0.2	1.7	6.3
	8	28	0.1	1.6	8.5
EQUILIBRIUM	11	0	0	1.5	11
ANIONIC RESIN	0	0	0	1.5	0
	1	22	0.5	2	1.4
	2	24	1	2.5	2.4
	2	53	1 5	2 9	2.9
	3	6	2	3.4	3.1
	3	12	2 5	3.9	3.2
	3	16	3	4.3	3.3
	3	20	3 5	4.8	3.33
	3	24	4	5.3	3.4
	3	28	4.5	5 7	3 5
	3	33	5	6.2	3.55
	3	39	5 5	6.7	3 65
	3	45	6	7 2	3.75
	3	51	6 5	7.6	3 85
	3	58	7	8.1	4
	4	8	7.5	8.6	4.1
	4	24	8	9	4.4
	4	52	8.5	9 5	4.9
	5	29	9	10	5 5
	6	0	9 5	10.4	6
	6	27	10	10.9	6 45
	6	43	10 5	11 4	6.7
	6	59	11	11.9	7
	7	17	11 5	12.3	7.3
	8	5	12	12.8	8.1
	15	0	12.7	13.5	15
	22	0	12 8	13.6	22
EQUILIBRIUM	40	0	12 8	13.6	40

TABLE 11

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 100F FOR
TEG WITH 20% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6 2	7 3	0
	0	8	5 5	6.7	0.13
	0	12	5	6 2	0 2
	0	17	4.5	5.7	0.28
	0	23	4	5 3	0 38
	0	28	3.5	4.8	0.5
	0	32	3	4.3	0.53
	0	35	2 5	3.9	0.58
	0	42	2	3 4	0.7
	1	1	1.5	2.9	1
	1	56	1	2 5	2
	5	4	0.5	2	5
	18	0	0.1	1 6	18
	33	0	0	1.5	33
EQUILIBRIUM					
ANIONIC RESIN	0	0	0	1.5	0
	1	58	0 5	2	2
	3	34	1	2 5	3.6
	4	42	1 5	2.9	4.7
	5	21	2	3 4	5 35
	5	28	2.5	3 9	5.5
	5	48	3	4.3	5.8
	5	55	3.5	4.8	5 9
	6	2	4	5 3	6
	6	10	4 5	5 7	6.2
	6	19	5	6 2	6 3
	6	28	5.5	6.7	6.5
	6	36	6	7 2	6.6
	6	46	6.5	7.6	6.8
	6	56	7	8 1	6.9
	7	8	7.5	8 6	7 1
	7	28	8	9	7.5
	7	57	8.5	9.5	7 95
	8	36	9	10	8.6
	9	9	9 5	10 4	9 15
	9	35	10	10 9	9 6
	9	59	10.5	11.4	10
	10	36	11	11.9	10 6
	12	10	11 5	12 3	12.2
	23	30	12	12.8	23 5
	45	0	12.05	12 8	45
	60	0	12 05	12.8	60
EQUILIBRIUM					

TABLE 12

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 100F FOR
TEG WITH 10% WATER USING ANION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6.2	7.3	0
	0	9	7	8.1	0.15
	0	17	7.5	8.6	0.28
	0	33	8	9	0.55
	0	59	8.5	0.5	0.98
	1	31	9	10	1.52
	2	0	9.5	10.5	2
	2	22	10	10.9	2.4
	2	34	10.5	11.4	2.6
	2	43	11	11.9	2.7
	2	56	11.5	12.3	2.9
	3	23	12	12.8	3.4
	4	33	12.5	13.3	4.5
	11	30	13	13.8	11.5
	18	0	13.1	13.83	18
EQUILIBRIUM	45	0	13.1	13.83	45
	0	0	13	13.8	0
	10	33	12.5	13.3	10.6
	14	52	12	12.8	14.9
	16	45	11.5	12.3	16.8
	17	34	11	11.9	17.6
	18	5	10.5	11.4	18
	18	34	10	10.9	18.6
	19	19	9.5	10.5	19.3
	20	45	9	10	20.8
	23	12	8.5	9.5	23.2
	26	20	8	9	26.3
	30	45	7.5	8.6	31
	34	45	7	8.1	34
	36	38	6.5	7.6	36.6
	37	50	6	7.2	37.8
	39	7	5.5	6.7	39.1
	40	14	5	6.2	40.2
	41	21	4.5	5.7	41.4
	42	20	4	5.3	42.3
	43	2	3.5	4.8	43
	43	36	3	4.3	43.6
	44	29	2.5	3.8	44.5
	46	42	2	3.4	46.7
	54	25	1.5	3	54.4
	74	30	1.2	2.6	74.5
EQUILIBRIUM	90	0	1.2	2.6	90

TABLE 13

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 100F FOR
TEG WITH 20% WATER USING ANION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6.2	7.3	0
	0	4	6.5	7.6	0.07
	0	9	7	8.1	0.15
	0	17	7.5	8.6	0.3
	0	33	8	9	0.55
	1	0	8.5	9.5	1
	1	34	9	10	1.6
	2	2	9.5	10.4	2
	2	24	10	10.9	2.4
	2	39	10.5	11.4	2.65
	2	51	11	11.9	2.85
	3	10	11.5	12.3	3.2
	3	57	12	12.8	3.95
	6	33	12.5	13.3	6.55
	16	50	12.8	13.6	16.8
EQUILIBRIUM	30	0	12.8	13.6	30
CATIONIC RESIN	0	0	12.8	13.6	0
	5	4	12.5	13.3	5
	11	34	12	12.8	11.6
	14	16	11.5	12.3	14.3
	15	26	11	11.9	15.4
	16	4	10.5	11.4	16
	16	37	10	10.9	16.6
	17	26	9.5	10.4	17.4
	18	55	9	10	18.9
	20	50	8.5	9.5	20.8
	22	50	8	9	22.8
	24	31	7.5	8.6	24.5
	26	4	7	8	26
	27	20	6.5	7.6	27.3
	28	19	6	7.1	28.3
	29	7	5.5	6.6	29.1
	29	54	5	6.2	29.9
	30	40	4.5	5.7	30.1
	31	27	4	5.3	31.5
	32	10	3.5	4.8	32.2
	32	46	3	4.3	32.8
	33	40	2.5	3.9	33.7
	35	35	2	3.4	35.6
	42	35	1.5	2.9	42.6
	67	40	1.2	2.6	67.7
EQUILIBRIUM	80	0	1.2	2.6	80

TABLE 14

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 120F FOR
TEG WITH 10% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6	7.2	0
	0	5	5.5	6.7	0.01
	0	11	5	6.2	0.18
	0	17	4.5	5.7	0.28
	0	22	4	5.3	0.37
	0	26	3.5	4.8	0.43
	0	30	3	4.3	0.5
	0	33	2.5	3.9	0.55
	0	36	2	3.4	0.6
	0	41	1.5	2.9	0.7
	0	59	1	2.5	1
	1	49	0.5	2	1.8
	3	45	0.1	1.6	3.8
EQUILIBRIUM	4	40	0	1.5	4.7
ANIONIC RESIN	0	0	0	1.5	0
	0	59	0.5	2	1
	1	35	1	2.5	1.6
	1	50	1.5	2.9	1.8
	2	1	2	3.4	2
	2	5	2.5	3.9	2.1
	2	7	3	4.3	2.12
	2	10	3.5	4.8	2.17
	2	14	4	5.3	2.2
	2	18	4.5	5.7	2.3
	2	22	5	6.2	2.4
	2	27	5.5	6.7	2.45
	2	31	6	7.2	2.52
	2	34	6.5	7.6	2.57
	2	37	7	8.1	2.62
	2	48	7.5	8.6	2.8
	3	6	8	9	3.1
	3	33	8.5	9.5	3.55
	3	57	9	10	3.95
	4	19	9.5	10.5	4.32
	4	37	10	10.9	4.62
	4	47	10.5	11.4	4.8
	4	57	11	11.9	4.95
	5	12	11.5	12.3	5.2
	5	53	12	12.8	5.9
	8	1	12.5	13.3	8
	19	17	12.8	13.5	19.3
EQUILIBRIUM	40	0	12.8	13.5	40

TABLE 15

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 120F FOR
TEG WITH 20% WATER USING CATION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC RESIN	0	0	6	7.2	0
	0	4	5.5	6.7	0.07
	0	9	5	6.2	0.15
	0	13	4.5	5.7	0.22
	0	17	4	5.3	0.28
	0	22	3.5	4.8	0.37
	0	25	3	4.3	0.42
	0	29	2.5	3.9	0.48
	0	32	2	3.4	0.53
	0	42	1.5	2.9	0.7
	1	9	1	2.5	1.15
	2	21	0.5	2	2.35
	5	15	0.1	1.6	5.25
	6	50	0	1.5	6.83
EQUILIBRIUM					
ANIONIC RESIN	0	0	0	1.5	0
	1	1	0.5	2	1.01
	1	39	1	2.5	1.65
	1	59	1.5	2.9	2
	2	7	2	3.4	2.12
	2	11	2.5	3	2.18
	2	14	3	4.3	2.23
	2	17	3.5	4.8	2.28
	2	20	4	5.3	2.33
	2	24	4.5	5.7	2.4
	2	27	5	6.2	2.45
	2	30	5.5	6.7	2.5
	2	34	6	7.2	2.57
	2	39	6.5	7.5	2.65
	2	44	7	8.1	2.73
	2	53	7.5	8.6	2.9
	3	9	8	9	3.15
	3	29	8.5	9.5	3.5
	3	50	9	10	3.83
	4	6	9.5	1.5	4.1
	4	22	10	10.9	4.37
	4	33	10.5	11.4	4.55
	4	46	11	11.9	4.77
	5	16	11.5	12.3	5.27
	6	42	12	12.8	6.7
	42	0	12.45	13.2	42
	60	0	12.45	13.2	0
EQUILIBRIUM					

TABLE 16

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 120F FOR
TEG WITH 10% WATER USING ANION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6	7.2	0
	0	7	6.5	7.6	0.12
	0	13	7	8.1	0.22
	0	23	7.5	8.6	0.38
	0	41	8	9	0.68
	1	6	8.5	9.5	1.1
	1	27	9	10	1.45
	1	46	9.5	10.4	1.8
	1	58	10	10.9	2
	2	5	10.5	11.4	2.1
	2	11	11	11.9	2.2
	2	24	11.5	12.3	2.4
	2	51	12	12.8	2.85
	4	4	12.5	13.3	4.1
	30	0	13.05	13.8	30
	45	0	13.05	13.8	0
EQUILIBRIUM					
CATIONIC RESIN	0	0	13	13.7	0
	8	29	12.5	13.3	8.5
	12	11	12	12.8	12.2
	13	53	11.5	12.3	13.9
	14	38	11	11.9	14.6
	15	1	10.5	11.4	15
	15	19	10	10.9	15.3
	15	47	9.5	10.5	15.8
	16	38	9	10	16.6
	18	15	8.5	9.5	18.3
	20	38	8	9	20.6
	23	34	7.5	8.6	23.6
	26	47	7	8	26.8
	28	44	6.5	7.6	28.7
	29	47	6	7.2	29.8
	30	37	5.5	6.7	30.6
	31	23	5	6.2	31.4
	32	16	4.5	5.7	32.3
	32	59	4	5.3	33
	33	28	3.5	4.8	33.5
	33	52	3	4.3	33
	34	23	2.5	3.9	34.4
	35	20	2	3.4	35.3
	37	59	1.5	2.9	38
	48	45	1	2.5	48.8
	55	50	0.9	2.4	55.9
EQUILIBRIUM					

TABLE 17

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 120F FOR
TEG WITH 20% WATER USING ANION TREATMENT FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	6	7.2	0
	0	5	6.5	7.6	0.01
	0	10	7	8.1	0.2
	0	17	7.5	8.6	0.3
	0	31	8	9	0.5
	0	53	8.5	9.5	0.9
	1	14	9	10	1.2
	1	29	9.5	10.5	1.5
	1	43	10	10.9	1.7
	1	51	10.5	11.4	1.85
	1	58	11	11.9	2
	2	12	11.5	12.3	2.2
	2	46	12	12.8	2.8
	4	44	12.5	13.3	4.7
	13	15	12.8	13.6	13.25
EQUILIBRIUM	30	0	12.8	13.6	0
CATIONIC RESIN	0	0	12.8	13.6	0
	3	43	12.5	13.3	3.72
	8	51	12	12.8	8.85
	11	12	11.5	12.3	11.2
	12	10	11	11.9	12.2
	12	40	10.5	11.4	12.7
	13	3	10	10.9	13.05
	13	27	9.5	10.5	13.45
	14	13	9	10	14.22
	15	31	8.5	9.5	15.5
	17	6	8	9	17.1
	18	51	7.5	8.6	18.85
	20	38	7	8	20.6
	21	59	6.5	7.6	22
	22	55	6	7.2	23
	23	35	5.5	6.7	23.6
	24	11	5	6.2	24.2
	24	48	4.5	5.7	24.8
	25	24	4	5.3	25.4
	25	58	3.5	4.8	26
	26	27	3	4.3	26.45
	27	1	2.5	3.9	27
	28	12	2	3.4	28.2
	32	6	1.5	2.9	32.1
	85	0	0.9	2.4	85
EQUILIBRIUM	100	0	0.9	2.4	0

TABLE 18

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 140F FOR
TEG WITH 20% WATER USING CATION TREATMENT FIRST

TIME		pH meter	pH corrected	TIME		$\ln(\text{pH}_0/\text{pH})$
min	sec			min		
0	0	5.6	6.8	0		0
0	5	5	6.2	0.08		0.09
0	8	4.5	5.7	0.13		0.18
0	11	4	5.3	0.18		0.25
0	14	3.5	4.8	0.23		0.35
0	17	3	4.3	0.28		0.46
0	19	2.5	3.9	0.32		0.56
0	21	2	3.4	0.35		0.69
0	25	1.5	2.9	0.42		0.85
0	35	1	2.5	0.58		1
1	4	0.5	2	1.1		1.22
2	5	0.1	1.6	2.1		1.45
2	35	0	1.5	2.6		1.51
EQUILIBRIUM						
0	0	0	1.5	0		0
0	56	0.5	2	0.94		0.04
1	17	1	2.5	1.28		0.08
1	27	1.5	2.9	1.45		0.12
1	32	2	3.4	1.53		0.16
1	35	2.5	3.9	1.58		0.21
1	37	3	4.3	1.62		0.25
1	39	3.5	4.8	1.65		0.3
1	42	4	5.3	1.7		0.36
1	45	4.5	5.8	1.75		0.42
1	48	5	6.2	1.8		0.47
1	50	5.5	6.7	1.83		0.54
1	53	6	7.2	1.9		0.6
1	57	6.5	7.6	1.95		0.67
2	4	7	8.1	2.1		0.75
2	14	7.5	8.6	2.23		0.84
2	28	8	9	2.5		0.92
2	46	8.5	9.5	2.77		1
3	1	9	10	3.02		1.14
3	15	9.5	10.5	3.25		1.27
3	25	10	10.9	3.42		1.4
3	33	10.5	11.4	3.55		1.57
3	44	11	11.9	3.73		1.78
4	13	11.5	12.3	4.22		2
5	51	12	12.8	5.85		2.34
6	40	12.1	12.9	6.67		2.43
14	0	12.3	13	14		2.43
30	0	12.35	13.1	30		2.53
55	0	12.35	13.1	55		2.53

TABLE 19

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 140F FOR
TEG WITH 20% WATER USING ANION TREATMENT FIRST

min	TIME sec	pH meter	pH corrected	TIME min	ln(pH ₀ /pH)
0	0	8	9	0	0
0	4	8.5	9.5	0.07	0.1
0	6	9	10	0.1	0.22
0	7	9.5	10.4	0.12	0.33
0	9	10	10.9	0.15	0.48
0	11	10.5	11.4	0.2	0.65
0	13	11	11.9	0.22	0.87
0	19	11.5	12.3	0.32	1.1
0	37	12	12.8	0.62	1.43
1	30	12.5	13.3	1.5	2
3	32	12.8	13.6	3.53	2.5
6	12	12.9	13.65	6.2	2.7
25	0	12.9	13.65	25	2.7
EQUILIBRIUM					
0	0	12.9	13.65	0	0
3	24	12.5	13.3	3.4	0.03
6	0	12	12.8	6	0.06
7	2	11.5	12.3	7	0.1
7	27	11	11.9	7.45	0.14
7	40	10.5	11.4	7.7	0.18
7	46	10	10.9	7.8	0.22
7	52	9.5	10.4	7.9	0.27
7	57	9	10	7.95	0.31
8	5	8.5	9.5	8.1	0.36
8	16	8	9	8.3	0.42
8	34	7.5	8.6	8.6	0.46
8	56	7	8.1	9	0.52
9	16	6.5	7.6	9.3	0.59
9	32	6	7.1	9.5	0.65
9	47	5.5	6.7	9.8	0.71
10	0	5	6.2	10	0.79
10	18	4.5	5.7	10.3	0.87
10	39	4	5.3	10.65	0.95
11	1	3.5	4.8	11	1.05
11	16	3	4.3	11.3	1.16
11	28	2.5	3.9	11.5	1.25
11	39	2	3.4	11.65	1.4
12	1	1.5	2.9	12	1.5
13	0	1	2.5	13	1.7
15	51	0.5	2	15.85	1.9
19	20	0.3	1.8	19.3	2
55	0	0	1.5	55	2.2
EQUILIBRIUM					

TABLE 20

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 140F FOR
TEG WITH 20% WATER USING CATION(AMBERLYST 15) FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
CATIONIC	0	0	7.3	8.4	0
RESIN	0	21	1	2.5	0.35
	0	32	0.5	2	0.53
EQUILIBRIUM	1	5	0	1.5	1.1
ANIONIC	0	0	0	1.5	0
RESIN	1	52	0.5	2	1.9
	3	19	1	2.5	3.3
	4	19	1.5	2.9	4.3
	5	2	2	3.4	5
	5	39	2.5	3.9	5.7
	6	26	3	4.3	6.4
	7	46	3.5	4.8	7.8
	10	16	4	5.3	10.3
	15	15	4.5	5.7	15.3
	70	0	5	6.2	70
EQUILIBRIUM	100	0	5	6.2	100

TABLE 21

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENT AT 140F FOR
TEG WITH 20% WATER USING ANION(AMBERLYST 21) FIRST

RESIN USED	TIME min	TIME sec	pH meter	pH corrected	TIME min
ANIONIC RESIN	0	0	7.1	8.2	0
	0	10	7.3	8.4	0.16
	0	15	7.4	8.5	0.25
	0	23	7.5	8.6	0.38
	0	33	7.6	8.66	0.55
	0	48	7.7	8.75	0.8
	1	6	7.8	8.85	1.1
	1	33	7.9	8.94	1.55
	1	58	8	9.04	2
	2	45	8.1	9.13	2
	3	48	8.2	9.22	3.8
	5	38	8.3	9.32	5.6
	9	20	8.4	9.41	9.3
	19	20	8.5	9.5	19.3
	49	0	8.6	9.6	49
	70	0	8.7	9.7	70
	95	0	8.8	9.8	95
	122	0	8.9	9.9	122
EQUILIBRIUM	160	0	9	10	160
	180	0	9	10	180
	200	0	9	10	0
CATIONIC RESIN	0	0	9	10	0
	0	4	8.5	9.5	0.07
	0	6	8	9.03	0.1
	0	9	7.5	8.6	0.15
	0	15	6	7.2	0.25
	0	19	5.5	6.7	0.32
	0	22	5	6.6	0.36
	0	25	4.5	5.7	0.42
	0	27	4	5.3	0.45
	0	31	3	4.34	0.52
	0	33	2.5	3.9	0.55
	0	37	1.5	2.9	0.62
	0	41	1	2.5	0.69
	0	46	0.5	2	0.77
	0	58	0.2	1.7	0.97
	1	7	0	1.5	1.12

TABLE 22

RATE CONSTANTS FOR BATCH EXPERIMENTS FOR TEG WITH 10%
AND 20% WATER AT DIFFERENT TEMPERATURES USING
ANION TREATMENT FIRST

EXP #	TEMP (deg F)	WATER % by VOLUME	RATE.CON (1/min)	LAG.TIME (min)
AT74W10	74	10	0.204	0
AT74W20	74	20	0.2524	0
AT100W10	100	10	0.4014	0
AT100W20	100	20	0.342	0
AT120W10	120	10	0.501	0
AT120W20	120	20	0.473	0
AT140W20	140	20	0.6823	0

TABLE 23

RATE CONSTANTS FOR BATCH EXPERIMENTS FOR TEG WITH 10%
AND 20% WATER AT DIFFERENT TEMPERATURES USING
CATION TREATMENT FIRST

EXP #	TEMP (deg F)	WATER % by VOLUME	RATE.CON (1/min)	LAG.TIME (min)
CT74W20	74	10	0.1588	0
CT74W20	74	20	0.4846	0
CT100W10	100	10	1.04	0
CT100W20	100	20	0.3314	0
CT120W10	120	10	0.4876	0
CT120W20	120	20	0.466	0
CT140W20	140	20	1.263	0

TABLE 24

RATE CONSTANTS FOR BATCH EXPERIMENTS FOR TEG WITH 10%
AND 20% WATER AT DIFFERENT TEMPERATURES USING
ANIONIC TREATMENT FOR CATION TREATED TEG

EXP #	TEMP (deg F)	WATER % by VOLUME	RATE.CON (1/min)	LAG.TIME (min)
AT74W10	74	10	0.04	32
AT74W20	74	20	0.03	29
AT100W10	100	10	0.04	14
AT100W20	100	20	0.07	17
AT120W10	120	10	0.05	12
AT120W20	120	20	0.05	8
AT140W20	140	20	0.23	6

TABLE 25

RATE CONSTANTS FOR BATCH EXPERIMENTS FOR TEG WITH 10%
AND 20% WATER AT DIFFERENT TEMPERATURES USING
CATIONIC TREATMENT FOR ANION TREATED TEG

EXP #	TEMP (deg F)	WATER % by VOLUME	RATE.CON (l/min)	LAG.TIME (min)
CT74W10	74	10	0.17	7
CT74W20	74	20	0.18	8.3
CT100W10	100	10	0.31	1.6
CT100W20	100	20	0.16	2.6
CT120W10	120	10	0.43	1.1
CT120W20	120	20	0.5	1
CT140W20	140	20	0.55	0.8

TABLE 26

ANALYSIS OF BATCH EXPERIMENT SAMPLES USING
ION-CHROMATOGRAPH AND EXPERIMENTAL
ERROR

EXP #	TEMP deg F	Cl- Ions Average	Concentration(ppm)	
			Minimum	Maximum
A_T74_W10	74	68	59	88
A_T100_W10	100	93	82	108
A_T120_W10	120	95	87	108
C_T74_W10	74	29	19	40
C_T100_W10	100	57	55	74
C_T120_W10	120	71	59	90
A_T74_W20	74	73	24	105
A_T100_W20	100	115	85	172
A_T120_W20	120	59	37	87
A_T140_W20	140	106	79	125
C_T74_W20	74	38	26	49
C_T100_W20	100	48	29	78
C_T120_W20	120	43	29	58
C_T140_W20	140	38	24	67

TABLE 27

VOLUME COLLECTED AND CONCENTRATION CHANGE WITH TIME
FOR 500ML TEG WITHOUT WATER HAVING AN INITIAL
CONCENTRATION OF 330ppm OF CHLORIDE IONS IN
A COLUMN EXPERIMENT USING 5.0gr OF CATION
AND ANION RESINS EACH WITH A RESIDENCE
TIME OF 2 MINUTES

SAMPLE #	TIME (MIN)	VOLUME (ml)	PEAK HEIGHT	CONC. OF Cl- (ppm)
0	0	0	0	0
1	5	22	1	15
2	10	38	0.9	10
3	15	54	0.75	4
4	20	69	0.55	0
5	25	84	0.35	0
6	30	99	0.3	0
7	35	114	0.4	0
8	40	129	0.4	0
9	46	148	0.45	0
10	50	160	0.5	0
11	55	175	0.6	0
12	60	190	0.7	2
13	65	205	0.8	6
14	70	220	0.9	10
15	75	236	1.1	17
16	80	251	1.2	21
17	85	267	1.3	28
18	90	282	1.45	35
19	95	298	1.5	37
20	100	314	1.6	41
21	105	331	1.9	55
22	110	347	2.2	68
23	115	363	2.35	74
24	120	379	2.55	83
25	125	394	2.8	94
26	130	409	3	102
27	135	424	3.1	107
28	140	439	3.35	118
29	145	453	3.5	125
30	180	488	3.5	81

TABLE 28

VOLUME COLLECTED AND CONCENTRATION CHANGE WITH TIME
 FOR 750ml TEG WITH 15% WATER HAVING AN INITIAL
 CONCENTRATION OF 330ppm OF CHLORIDE IONS IN
 A COLUMN EXPERIMENT USING 5.0gr OF CATION
 AND ANION RESINS EACH WITH A RESIDENCE
 TIME OF 2 MINUTES

SAMPLE #	TIME (MIN)	VOLUME (ml)	PEAK HEIGHT	CONC. OF Cl- (ppm)
0	0	0	0	0
1	5	23	0	0
2	10	43	0	0
3	30	123	0	0
4	35	143	0	0
5	40	163	0	0
6	45	183	0.1	0
7	50	203	0.18	0
8	55	223	0.2	0
9	60	243	0.25	0
10	65	263	0.3	0
11	70	282	0.4	0
12	75	301	0.4	0
13	80	319	0.55	0
14	85	336	0.6	0
15	90	354	0.7	2
16	95	372	0.75	4
17	100	390	0.9	10
18	105	408	1	15
19	110	426	1.15	21
20	115	444	1.3	28
21	120	462	1.55	39
22	125	479	1.7	46
23	130	496	1.9	55
24	135	513	2.05	61
25	140	530	2.25	70
26	150	564	2.5	81
27	160	598	2.95	101
28	170	632	3.25	110
29	180	664	3.7	134
30	190	696	4.1	151
31	200	726	4.5	169
32	210	756	4.7	178
33	220	786	4.5	189
34	230	812	5.2	200
35	240	837	5.5	213
36	250	860	5.5	213
37	270	875	5.5	213

TABLE 29
ION-CHROMATOGRAPH CALIBRATION

CONCE OF Cl- (PPM)	PEAK.HT (CM)
0.1	0.16
0.25	0.4
0.5	1
0.75	1.45
1	1.85
2.5	4.2
5	10.2

TABLE 30

pH CHANGE VERSUS TIME FOR BATCH EXPERIMENTS AT 74F FOR
TEG WITH 20% WATER USING WET, SOAKED, AND DRY
CATIONIC RESINS FIRST

pH	Wet resin	Time in Min Soaked resin	Dry Resin
7.7	0	0	0
7.5	0.37	0.27	0.2
7	0.83	0.63	0.68
6.5	1.3	1.05	1.13
6	1.7	1.42	1.53
5.5	2.02	1.75	1.85
5	2.33	1.98	2.12
4.5	2.6	2.23	2.35
4	3	2.55	2.67
3.5	4.15	3.32	3.48
3	8.05	5.07	6.27
2.5	24.2	17.17	17.67
2.4	35	24.5	25
Equilibrium			
2.4	0	0	0
2.5	0.88	2.37	2.33
3	3.92	6.4	6.33
4	7.33	10.98	11.58
5	8.15	12.57	13.45
6	8.87	13.52	14.85
7	9.67	14.75	16.73
8	10.5	15.95	19.07
9	11.4	17.25	22.83
10	12.88	19.17	30.08
11	14.78	21.73	44.87
11.5	15.45	22.7	70
Equilibrium			

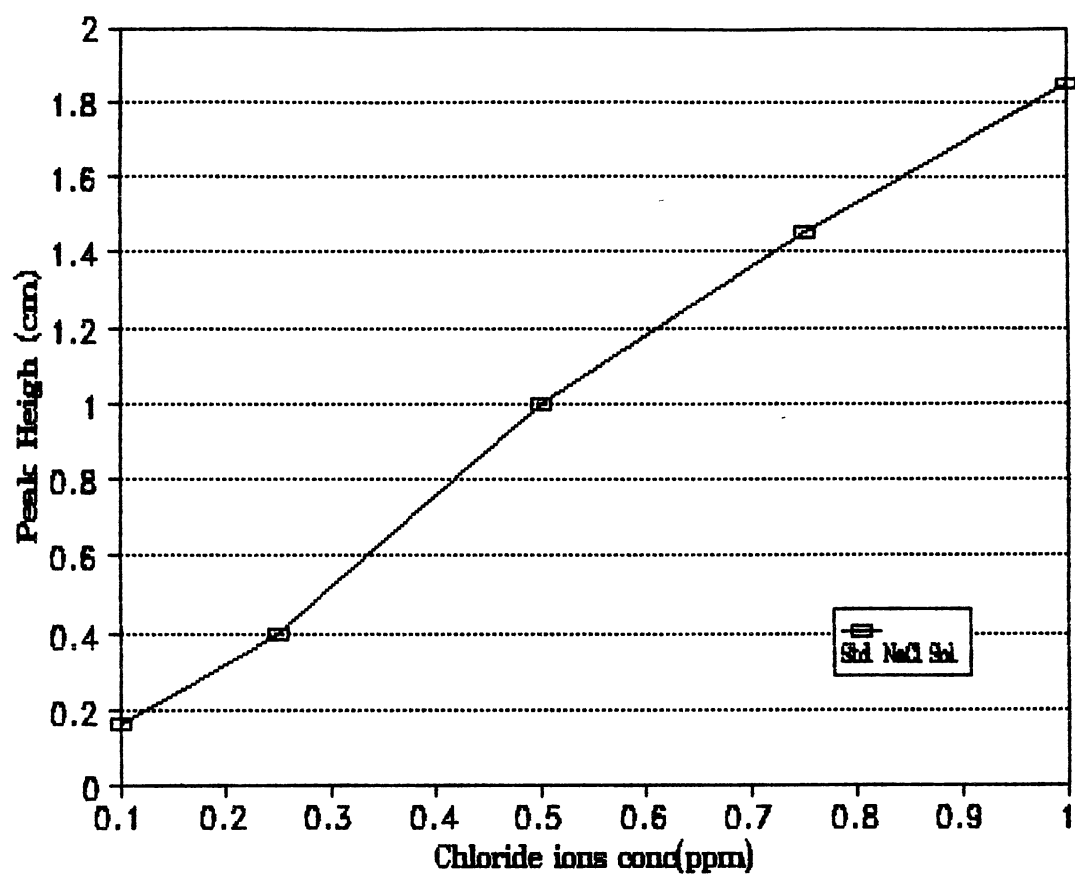


Figure 18. Ion-Chromatograph Calibration

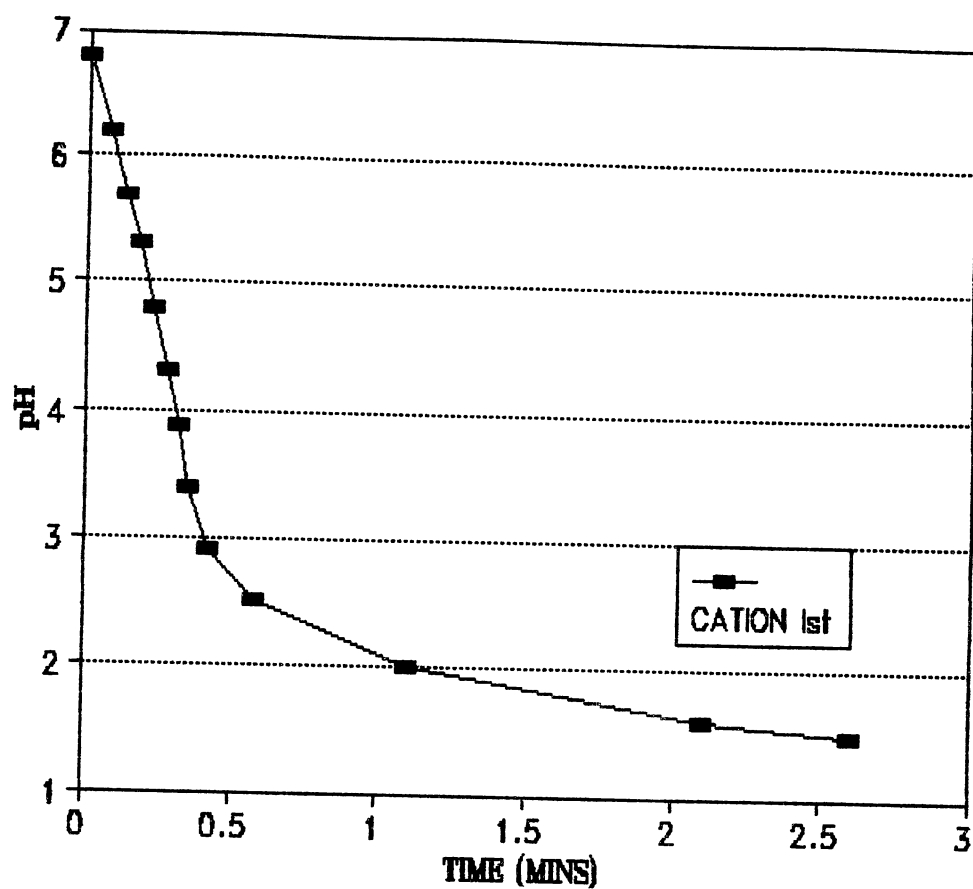


Figure 19. pH Change Versus Time For Batch
Experiment For TEG With 20% Water
At 140°F Using Cation Treatment
First

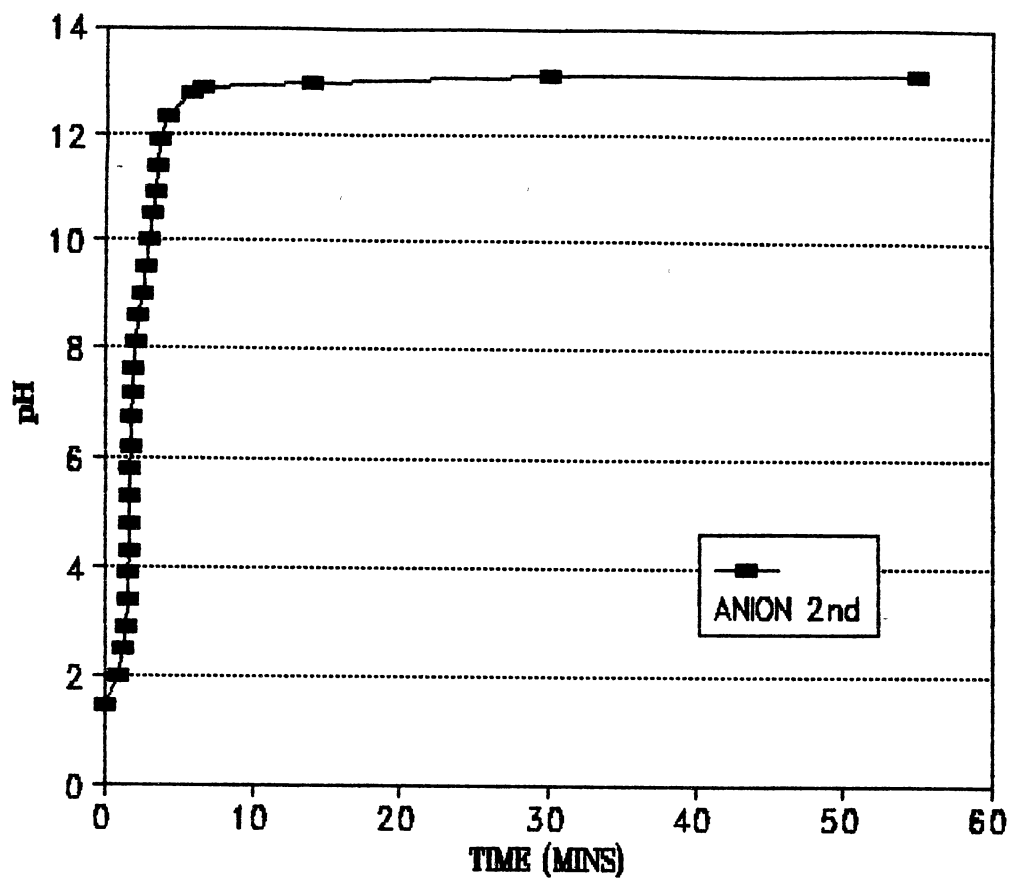


Figure 20. pH Change Versus Time For Batch
Experiment For TEG With 20% Water
At 140°F Using Anion Treatment For
Cation Treated Solution

APPENDIX B
EQUIPMENT SIZING AND COST ESTIMATION

EQUIPMENT SIZING AND COST ESTIMATION

The equipment sizing and cost estimation for the design of ion-exchange process at 180°F are given below. No data is available at 180°F, but the preliminary experiments show little or no effect with temperature on the ion-exchange process.

(i) Cation Exchanger:

Assuming a residence time of 2 min at 180°F (from Experiment C_T140_W20):

TEG flow rate = 30 gpm = 0.06684 ft³/sec.

Void Volume of resin bed = 120 x 0.06684 = 8 ft³

Assuming a 40% void volume present in the resin bed:

Volume of resin required = 8/0.4
= 20 ft³

Assuming the resin is half full in the cation exchanger

Volume of cation exchanger = 40 ft³

Assuming a maximum resin bed depth = 36 inches

which gives a diameter of the cation exchanger about 3 ft

the material of construction is chosen to be stainless steel.

D = 3 ft; L = 6 ft.

cost = (897/256) x \$2500 (897,M and S equipment cost index
1989 third quarter)

= \$9000

Velocity through the column = 0.0095 ft/sec.

(ii) Anion Exchanger:

From column experiments Residence time = 1.7 min

Therefore choosing a residence time about 2 min.

Void volume of resin bed = 8 ft^3 .

Volume of resin required = $(8/0.4)$

= 20 ft^3 .

Volume of anion exchanger = 40 ft^3 .

Diameter of anion exchanger = 3 ft.

Length of anion exchanger = 6 ft.

Material of construction: stainless steel

Cost = $(897/256) \times 2500$

= \$9000

(iii) Volume of Regenerants:

The volume of regenerant should be sufficient to fill the void volume of the resin bed = 8 ft^3 . Therefore, assuming a regenerant volume required of approximately 10 ft^3 .

Volume of acid regenerant = 10 ft^3 .

Volume of caustic regenerant = 10 ft^3 .

(iv) Acid and Caustic Tanks:

Volume of acid regenerant required = 10 ft^3 .

The acid and caustic can be stored in 55gal HDPE tanks.

Material of construction: HDPE

Cost (4 X 55gal tanks) = 4×165

= \$660

(v) Heat Exchanger:

A heat exchanger will be placed immediately after the charcoal filter, in the process stream, to reduce the process stream temperature from 220⁰F to 180⁰F. The heat exchanger will be a double pipe, counter flow exchanger.

The solvent TEG properties are evaluated at an average temperature of 200⁰F

(a) Solvent Density:

Density of water at 200⁰F = 59.8 lbm/ft³

Density of TEG at 200⁰F = 64.0 lbm/ft³

Assuming the solvent TEG contains 15% water Solvent density

$$= 64.0 \times 0.85 + 59.8 \times 0.15$$

$$= 63.4 \text{ lbm/ft}^3$$

(b) Solvent Specific Heat:

Specific heat of TEG at 200⁰F = 0.53 btu/lb ⁰F

Specific heat of water at 200⁰F = 1.0 btu/lb ⁰F

Solvent Specific Heat = 0.85x0.53 + 0.15x1.00

$$= 0.60 \text{ btu/lb } ^0\text{F}$$

(c) Solvent Viscosity:

Viscosity of TEG at Room Temperature = 45 cp

Viscosity of TEG at 200⁰F = 4.5 cp

Viscosity of Water at 200⁰F = 0.29 cp

There fore Viscosity of solvent = 0.85x4.5 + 0.15X0.29

$$= 0.0026 \text{ lb/sec ft}$$

Choosing a 1.5 inch NPS, Se 40, Steel pipe for the heat exchanger,

Inside Diameter $D_i = 1.61 \text{ inch} = 0.134 \text{ ft}$
 Area of crossection of pipe $A_i = 0.0141 \text{ ft}^2$
 TEG flow rate $= 30 \text{ gpm}$
 $= 0.06685$
 $= 4.24 \text{ lbm/sec}$
 Velocity through the pipe $V = 4.73 \text{ ft/sec}$
 There fore Reynolds number

$$\begin{aligned}
 N_{Re} &= D_i \times V \times \text{density} / \text{viscosity} \\
 &= 1.54 \times 10.0E4
 \end{aligned}$$

which is in turbulent flow.

No data is available for the thermal conductivity of TEG. So a rough estimation of overall heat transfer coefficient is taken.

From (17), the overall heat transfer coefficient for heavy organics in turbulent flow range is 75-125 Btu/hr ft²°F. estimating an overall coefficient of about 75 Btu/hr ft²°F

$$\begin{aligned}
 \text{Heat required} &= 4.24 \times 0.60 \times (220 - 180) \\
 &= 366154.6 \text{ Btu/hr}
 \end{aligned}$$

Cooling Water:

Assuming water enters at 75°F and leaves at 85°F

$$\text{Amount of water required} = \frac{366154.6}{1.0 \times (85 - 75)} = 72 \text{ gpm}$$

LMTD:

$$\text{LMTD} = \frac{(220 - 85) - (180 - 75)}{\ln(135/105)} = 120^\circ\text{F}$$

Area of Heat Exchanger:

$$A_o = \frac{Q}{U_o \times \text{LMTD}} = \frac{366154.6}{75 \times 120} = 40.7 \text{ ft}^2$$

Heat Exchanger Configuration:

Heat Exchanger Type	Double Pipe Heat Exchanger
Inner Tube (TEG)	1.5 in Se 40, steel pipe
Outer Tube (Water)	4.0 in , carbon pipe
Area of Heat Exchanger	40.7 ft ²
Length of Heat Exchanger	20ft (5 x 20)
Velocity of TEG in Tube	4.72 ft/sec

Pressure Drop Through Exchanger:

$$\text{Pressure drop} = \frac{2 \cdot f \cdot \text{Density} \cdot V^2 \cdot L}{D_i \cdot g_c}$$

$$\text{Friction factor} = 0.007$$

$$\text{Pressure drop} = 441.8 \text{ lb}_f/\text{ft}^2 = 3.2 \text{ psi}$$

which is within design limits.

Cost:

$$\text{Double Pipe Heat Exchanger (surface area)} = 101 \text{ ft}^2$$

$$\text{Cost} = \$ 6000$$

(vii) Pumps:

Two 1HP centrifugal pumps are required.

Cost:

$$1 \text{ HP, centrifugal pumps} = \$ 2000$$

APPENDIX C
CALCULATION OF RUN TIME

CALCULATION OF RUN TIME

From column run breakthrough curves, 5.0 gr of resin treated 450ml of TEG. The TEG initial Cl-concentration is approximately 330 ppm.

1 gr of resin exchanged 0.02745 gr of Cl-

But actual capacity of resin = 1.3 meq/ml = 4.8 meq/gr

$$= 4.8 \times 10.0 \times 35.5$$

$$= 0.1704 \text{ gr of Cl- / gr of Resin}$$

Therefore effective capacity of the resin

$$= 0.027 / 0.17$$

$$= 16 \%$$

Frequency of regeneration.

Volume of TEG = 48,000

$$= 1.81 \times 10^8 \text{ ml}$$

Volume of Resin = 20 ft³

$$= 5.66 \times 10^5 \text{ ml}$$

First Run Time:

About 825 ppm of salts were accumulated in the TEG over eight years. So, assuming approximately 100 ppm of NaCl is accumulated every year:

$$\begin{aligned} \text{First Run Time} &= \frac{1.3 \times 10^{-3} \times 35.5 \times 5.66 \times 10^5}{\frac{825(35.5/58.5) \times 1.81 \times 10^8}{10^6}} \\ &= 0.29 \text{ years} \end{aligned}$$

ACTUAL FIRST RUN TIME

$$\begin{aligned}\text{Actual First Run Time} &= 0.29 \times 0.16 \text{ years} \\ &= 17 \text{ Days Approximately}\end{aligned}$$

But subsequent regenerations will be longer, since the feed concentration will not be more than 25ppm of NaCl, and about 100ppm of NaCl is accumulated every year.

Therefore subsequent run times

$$\begin{aligned}&= \frac{1.3 \times 10^{-3} \times 35.5 \times 5.66 \times 10^5}{\frac{100(35.5/58.5) \times 1.81 \times 10^8}{10^6}} \\ &= 2.4 \text{ years}\end{aligned}$$

$$\begin{aligned}\text{Actual run time} &= 2.4 \times 0.16 \text{ years} \\ &= 5 \text{ months approximately}\end{aligned}$$

APPENDIX D
EXPERIMENTAL ERRORS

EXPERIMENTAL ERRORS IN THE ANALYSIS OF TEG SAMPLES

Experimental errors during the batch experiments

Potential errors may arise due to the following.

- (1) Weighing of resin
- (11) Measuring the TEG sample (volume)
- (111) Error in the pH meter

Since five times excess resin is taken for the batch experiments, these errors may effect the rate constant but not the residual salt content. So these errors are neglected.

Errors in the analysis of samples by IC

(1) Errors due to the preparation of standard solutions

Error in weighing NaCl

For 800 ppm of Cl⁻ 0.6592 gr/500 ml

This can be 0.65920 gr - 0.65929 gr

Volumetric error is +/- 5%

so 500 ml of water can be 475 ml to 525 ml

Therefore possible Cl⁻ ion concentration range for 800 ppm is

$0.6592/58.5 * 35500/525 * 1000 = 766$ ppm of Cl⁻

$0.659299/58.5 * 1000/475 * 35500 = 842$ ppm of Cl⁻

This has been diluted to 1 ppm - 0.1 ppm

The error in diluting to 1 ppm is

i.e., 1 ml of 800 ppm/800 ml of water

Therefore Range of concentration due to error may be $0.95/840$ to $1.05/760$

Therefore minimum concentration is

$$0.95/840 * 766 = 0.866 \text{ ppm}$$

The maximum concentration is

$$1.05/760 * 842 = 1.164 \text{ ppm}$$

Therefore Error % in standards is approximately -13.4% to 16.4%

(11) Error in diluting TEG samples

TEG samples are diluted to 1% i.e., 5 ml/500 ml water. So the possible error range is -9.52% to 10.52%.

Error From Ion-Chromatograph

Each sample is injected 7 times to take the average peak height. The actual peak height might lie between the lowest and the highest of 7 peak heights. The IC peak heights for all the samples are tabulated in table 30

The overall experimental error bar is calculated combining all these

TABLE 31

AVERAGE, MINIMUM, AND MAXIMUM PEAK HEIGHTS OF THE TEG
SAMPLES IN THE ANALYSIS USING ION-CHROMATOGRAPH

EXP #	Peak Height (cm)		
	Average	Minimum	Maximum
AT74W10	1.24	1 1	1.45
AT100W10	1 44	1.3	1 6
AT120W10	1.46	1.35	1.6
CT74W10	0.93	0 75	1.1
CT100W10	1.15	1 1	1.35
CT120W10	1.3	1 1	1.47
AT74W20	1.3	1.15	1.45
AT100W20	1.62	1.5	1.83
AT120W20	1 17	1.05	1.25
AT140W20	1.55	1 25	1.75
CT74W20	1	0 85	1.13
CT100W20	1 1	1.0	1.15
CT120W20	1	0 9	1.15
CT140W20	1	0 95	1.1

VITA

SUDHAKAR KALAGA

Candidate for the Degree of

Master of Science

Thesis: DESIGN AND COST ESTIMATION FOR DESALTING
TETRAETHYLENE GLYCOL USING ION-EXCHANGE

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Kakinada, India, August 20,
1966, the son of K.Srihari Rao and K.Subbalakhshmi

Education: Graduated from Rajbhavan Governament High
School, Hyderabad, India, in March 1981;
completed Pre-Engineering from St. Alphonsa's
Junior College, Hyderabad, India, in April 1983;
received Bachelor of Technology Degree in
Chemical Engineering from Osmania University,
Hyderabad, India, in May 1989; completed
requirements for the Master of Science Degree at
Oklahoma State University in December, 1990.

Professional Experience: Research Assistant, School
of Chemical Engineering, Oklahoma State
University, August, 1989, to December, 1990.